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TABLE OF CONTENTS — OCTOBER 1952

THE PRESENT STATUS OF THE DIRECT NEGATIVE-POSITIVE COLOR PROCESSES IN EUROPE

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The development of direct color printing methods cannot yet by any means be considered finished. It may be assumed that the technical details of the advances in this field in America up to the present time are familiar to all readers of this publication. It may be of some interest, therefore, to discuss the four different processes which have been developed in Europe during the last about fifteen years.

A certain relationship in image structure exists between the American processes of Kodacolor and Plenacolor on one hand and the following European processes on the other:

> Agfacolor
> Gevacolor
> Ferraniacolor
> Telcolor

With any of these processes it is possible to obtain results of high quality if all conditions essential for a satisfactory balance between negative and positive have been fulfilled.

All methods to be described have the following in common: As the first step a color negative is generated in the camera in an integral tripack material. Its colors are essentially complementary to those of the subject. After the negative material has undergone a special development, any number of colored paper pictures of the same subject can be made on a positive material of similar layer structure by a suitable printing and color development procedure.

With regard to the historical development, the following data appear to have been established:

(1) Already in 1933 the technical possibilities in theory and experiment existed, and these investigations were carried out largely in the plants of Agfa.

(2) The colored paper picture of today has evolved from the procedure for producing motion picture color films, printed from color negatives, with suitably modified details.

(3) Due to the particular conditions of the war and afterwar years these Agfa methods have been taken over and further developed by other manufacturers.

Prior to the development of the processes described here it was necessary for the making of a colored paper print to start with black-and-white separation negatives and combine the separation positives (derived from them in the three primary colors) during the printing process by special methods so that a paper picture in natural colors

* Swedish Colorphoto Corporation, Stockholm 1, Sweden. Received 9 July 1952. Translated from the original German by G. A. Wiesehahn.

could be obtained as the final result. The best known techniques, still much used today, are:
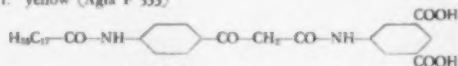
> Carbro
> Dye-transfer
> Duxochrome

and their modifications. All these processes are—due to inherent causes of defects—expensive to carry out and therefore suitable for certain special purposes only. There had been therefore much demand for direct methods for the preparation of pictures in natural colors. The methods employing color transparencies and a following color reversal procedure, such as Ansco Printon, offered a certain possibility in this direction. However, there was no corresponding process available in Europe.

The method using a negative in complementary colors has become today the starting point for a generally applicable procedure. Although the American production figures can hardly be attained in Europe, the four makes mentioned above have obtained overall results which are qualitatively as well as quantitatively very favorable. It is our task in the following to discuss the operation of the four processes with respect to both their physical and chemical characteristics and their phototechnical execution.

The negative films which are used as starting material for the paper print processes to be described all have a layer structure which is very similar to that of the tripack reversal films. However, in order to obtain satisfactory print results there must be differences in the gradation as compared with the reversal film. The conventional arrangement is followed in all cases. The uppermost layer is sensitive for blue only. Then follows a yellow filter layer. The second emulsion layer is green sensitive. The third one is sensitive to red.

These three layers contain the corresponding color-forming components. To the blue-sensitive layer there is therefore added a coupler which produces a yellow dye during color development. In the second layer there is the color former for a magenta dye, and in the third one for cyan. The three layers are treated with a common color developer. Whereas in the Kodacolor process the couplers are distributed by physical binding in the form of fine colloidal particles through the emulsion, increase of molecular size by the chemical attachment of long chains has been chosen in all European products to inhibit the diffusion of the couplers in the chromogenic development process. Typical representatives of the many patented color formers for the basic colors yellow, magenta, and cyan (FIAT Final Report #721) are the following:

1. yellow (Agfa F 535)

$$H_{35}C_{17}-CO-NH-\bigcirc-CO-CH_2-CO-NH-\bigcirc \genfrac{}{}{0pt}{}{COOH}{COOH}$$

II. magenta (Agfa Z 169)

H_3C—C—$C_{17}H_{35}$

(chemical structure diagram)

...SO_3H

III. cyan (Agfa F 546)

OH

...CO—NH—$C_{18}H_{37}$

SO_3H

The developing agent N,N-diethyl *p*-phenylenediamine, which is also known as *p*-aminodiethylaniline, is used in most cases. This compound,

H_5N—(benzene ring)—N—C_2H_5 / C_2H_5
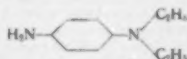
stains and irritates the skin. For this reason many attempts have been made to achieve improvements by the introduction of substituents. Success has been achieved, among others, by the introduction of a hydroxyl group into one of the ethyl groups of the molecule:

H_5N—(benzene ring)—N—C_2H_5 / $C_2H_4(OH)$
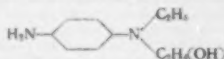
We shall discuss below other components which are present in a typical color negative developer.

The products formed in the negative films during development consist of dyes and it is possible to obtain in this manner, in the printing process, a generally satisfactory color reproduction. Nevertheless in two of the negative processes dealt with here (Ferraniacolor and Telcolor) it has been preferred, in order to improve the quality of the color reproduction and of the gradation, to convert part of the image silver, after completion of the color development and bleaching of the simultaneously formed image silver, to a black-and-white silver mask. In the other process (Agfacolor and Gevacolor) the image silver formed during the development reaction is completely removed by bleaching and fixation. This should be emphasized because in one of the American negative processes (Kodacolor) a colored mask is generated during the processing.

Agfacolor Negative Film

The Agfacolor Negative film is commercially available with a daylight and an artificial light emulsion. The daylight emulsion is sensitized for an average color temperature of 5,800K, the artificial light film for 3,200K. Assuming a normal development, the sensitivity of the daylight film is equivalent to an ASA Exposure Index of 16. The sensitivity of the artificial light film is about ASA 25. It is possible, by prolonging the developing time, to increase the sensitivity considerably at the expense of the gradation. However, an increase of the developer temperature cannot be recommended because of the risk of reticulation at elevated temperatures.

The Agfacolor material is sold in various sizes: 35mm magazines, originally in the length of 36 frames, now with 20 only; Karat magazines for 12 exposures; Roll film sizes 120 and 620. Besides there exists roll film 4.5cm wide. Sheet films are available in all sizes from $2^1/_4 \times 3^1/_4$ to 10×12 inches (24 × 30 cm).

These data pertain to the Agfacolor negative film which is produced by the Leverkusen plant in the Western zone of Germany, where the manufacture was taken up only about four years ago. In addition considerable quantities of the same film type, but of different properties, are being made in the original film factory of Agfa in Wolfen, now called Fotoplenka under Russian control. Originally the shelf life of the different emulsion types was one year after the date of manufacture. However, it was recently increased to two years.

In this connection it may be mentioned that the keeping quality of the latent image is not very long; so the development of the exposed film should be carried out within at most three months after the exposure. Otherwise there may be shifts in the proportionality of the three layers which can no longer be compensated for in the printing process. That the films should be stored cool and protected against the effect of chemically active gases is as valid here as with all color reversal films. The keeping quality under tropical conditions is uncertain.

Gevacolor Negative Film

The Gevacolor Negative film is available only as daylight emulsion for the $2^1/_4 \times 3^1/_4$ inch size on 120 spools. An emulsion for tungsten light has not appeared so far nor a 35mm emulsion in daylight loading magazines. So far the 35mm film exists only as artificial light emulsion and in lengths required for the taking of motion picture negatives whose popularity is constantly increasing in Europe. The manufacture of sheet films in different sizes is being prepared at the present in the Gevaert plant in Mortsel near Antwerp. The development of improvements of these materials is carried out there constantly and intensively.

Ferraniacolor Negative Film

The Ferraniacolor film, originating in Turin, Italy, is available so far in the 35mm size for 20 exposures. The $2^1/_4 \times 3^1/_4$ inch size film is also available. Both sizes are furnished only with daylight sensitization. Nothing is known up to now of sheet films.

Telcolor Negative Film

The firm of Tellko in Fribourg, Switzerland, sells the Telcolor film. This is sensitized as a universal film which permits the taking of exposures on the same material in daylight as well as artificial light. The 35mm films are available in magazines for 20 exposures, the $2^1/_4 \times 3^1/_4$ inch film in the 120 size for 8 exposures. Sheet film is also available.

The practical speed of Gevacolor daylight film is given as 24° Scheiner corresponding to ASA Exposure Index 16 with standard development. It too can be increased by prolonging the development time. Thus the speed of both Agfacolor and Gevacolor negative is higher by one half to one full stop than that of the corresponding color reversal films. The sensitivity of Ferraniacolor and Telcolor, however, is the very same as the usual speed of color reversal films, which are not being produced by these two manufacturers. This somewhat lower speed is related to the mask development of the two film types.

Use of Optical Filters

The use of filters during the exposure is to be avoided with all negative film types, because the resulting color shifts cannot be compensated during the printing process. Only haze filters are permissible. On the basis of the color temperature for the sensitization only blue-colored flashlamps of the same type as for color reversal films are suitable as flashlamps for daylight type negative film.

Considering the developing procedure proper of the four negative films, and disregarding the necessary rinses shown in Table I, all materials described above have four steps in common:

1. Developer
2. Stop bath
3. Bleach bath
4. Fixing bath

The film makes described here can be divided into two groups: those in which the process is carried out as above, and those in which an additional black-and-white mask is introduced by an additional black-and-white development after the bleach. Agfa and Gevaert films form the first, Ferrania and Tellko films the second group.

It is remarkable that the classical processes of this technique even today still operate without masks, whereas those which arrived later

Table I.

NEGATIVE PROCESSING TIME TABLE

	Step	Agfa	Gevacolor	Ferrania	Telcolor
1.	Development	6' 18C	10' 20C	7' 18C	6' 18C
2.	Hardening	2'	..	..	..
3.	Rinse	10'	10"	20'	15'
4.	Stop Bath	..	5'	..	..
5.	Rinse	..	30'	..	..
6.	Bleach	3'*	5'*	5'*	5'*
7.	Rinse	3'	30'	10'	10'
8.	Fixing	3'	5'	5'	5'
9.	Rinse	20'	5'	20'	20'
10.	Stabilization	..	5'	..	..
11.	Rinse	..	20'	..	..

* End of darkroom processing.

Table II.

MASK PROCESSING TIME TABLE

	Steps Following the Bleach	Ferraniacolor	Telcolor
1.	Rinse	10'	10'
2.	Exposure with 10 lux of white light	(from base side)	(from emulsion side)
3.	Mask development (density of the silver mask 0.4)	3'	3.5'
4.	Rinse	5'	5'
5.	Fixing	5'	5'
6.	Final rinse	20'	20'

obtain even better color separation by the masking principle. Tellko, for example, leaves the alternative of operating without mask in its directions and gives as the reason that the development of the silver mask is not without certain technical difficulties. A critical second exposure is required which, with the use of the prescribed mask developer, should produce a density of exactly 0.4 measured on the unexposed image edge.

Practical experiments have shown that the color separation in this manner is undoubtedly improved; but it is questionable, whether this improvement is worth the considerably greater amount of work required.

Processing Agfacolor Film

The following formulas for the development of the Agfacolor films are typical of formulas for color negative films. The formulas have not been published by the manufacturer because of the restrictive policies of this firm.

Developer

p-aminodiethylaniline hydrochloride	2.1 g
Hydroxylamine hydrochloride	1.2 g
Potassium carbonate	75.0 g
Sodium sulfite, anhydrous	2.0 g
Potassium bromide	2.5 g
Sodium hexametaphosphate	1.0 g
Water to make	1.0 l

Hardening Bath

Magnesium sulfate	20 g
Water to make	1 l

Bleach

Potassium ferricyanide	40 g
Potassium bromide	30 g
Water to make	1 l

Fixing Bath

Sodium thiosulfate	300 g
Borax	5 g
Water to make	1 l

The normal developing time of 7 minutes at 18C can be varied between 6 and 9 minutes if known over- or underexposures have to be compensated for. However, underdeveloped color negatives always produce poorer print results than those which are somewhat overexposed or overdeveloped. With still longer developing times the results become too hard. This is obvious not only in unpleasant image contrast but also in the fact that halation may appear in the paper print.

The temperature of 18C is very critical for the Agfacolor developer and must not be exceeded by more than 1° without running into the danger of loosening of the layers or of reticulation of the gelatin. The other makes mentioned are less sensitive in this respect. Consequently they do not require a special hardening bath. The density curves are influenced by increasing the temperature as well as by increasing the time in color development the same as in black-and-white development. For uniform results the 18C temperature should be

maintained ±1°. For this type of color developers the rise occurs rather rapidly. This is due to two causes:

1. the high alkali content of the developer
2. the content of hydroxylamine.

The last mentioned substance has proven itself as a development accelerator as well as antifoggant in all color negative and color paper processes. It may be recalled in this connection that it also is being used in the color developer for Ansco Printon material. The dosage of the hydroxylamine as well as that of the potassium bromide is extremely critical. The following hardening bath—the only one of all the processing baths whose composition has been published by Agfa—is recommended only for soft water but has proven very important in all cases in order to avoid reticulation.

The duration of the following rinse as well as its temperature is of great importance; for the action of the color developer is not immediately stopped in the recommended processing. Instead the film, saturated with solution, continues to develop during the washing. Simultaneously the residual developing agent diffuses out of the layer. The slow diffusion produces a softer result in the negative development which is important for the later printing process in the use of the Agfacolor film. Furthermore the full speed of the film is made use of only with this washing.

The rinsing must last for at least 10 minutes. With a shorter wash a disturbing color reaction occurs afterward in the bleach bath which stains the negative films making them unsuitable for the production of a neutral color balance in printing. This magenta dye occurs as the oxidation product of the color developing agents with the potassium ferricyanide of the bleach bath and stains the gelatin substantively. It cannot be washed out or destroyed by a chemical aftertreatment. The formation of this fog dye is about proportional to the duration of the intermediate rinse, and after 10 minutes has reached a point where the color fog is practically on a nonmeasurable level.

In the following bleach bath the silver, which has been formed during development besides the dye, is converted to silver ferrocyanide and silver bromide. Both are substances which easily dissolve in the subsequent final fixing bath. The duration of the washing following the bleach is only of importance insofar as a somewhat prolonged rinse can extend the use of the fixing baths before renewal becomes necessary. The composition of the bleach bath for films of this type is not very critical, but impurities in the potassium ferricyanide supply may cause variations in the pH value which in such a case should be maintained at 6.0 to 6.3 by a disodium phosphate-sodium bisulfate buffer.

The results of the negative development with Agfacolor as well as with the other negative films reveal considerable deviations in the color balance from the theoretical so that the basal character of the emulsion appears sometimes brownish, sometimes greenish, reddish, but only rarely neutral gray. This color tint is noticeable especially in the background fog but extends over all developed colors. The cause is the technical impossibility of manufacturing several emulsion coatings uniformly, conditions which are long familiar with color reversal film.

In the course of several years of manufacture some of the color formers have been replaced by better ones. However, the color tint of the negative emulsions is not of major importance because it always can be corrected by the use of filters in the printing process. One important reservation must be made: the emulsion to be developed must not have passed the date of expiration. If this is the case, the characteristic curves of the three color emulsions for a developed gray wedge are shifted so that they no longer run parallel to each other. Then a satisfactory neutral reproduction can no longer be expected in the printing process.

Besides the dreaded reticulation, due to insufficiently hardened emulsion, dry spots in the form of irregular lime deposits may be mentioned as a defect that may occur. They may be found when the

sodium hexametaphosphate recommended in the above developer formula is left out. In its place Calgon can be used. Under no circumstances should chamois or sponges be used in the drying; the danger of scratching the layer is too great and retouching in the print in many cases is impossible.

There is a considerable difference in the general behavior of the films originating in the Eastern zone compared with those from the Western zone. In the former the background fog is usually much greater, and the film support is of a different type. It is thicker and consists of nitrate film in contrast to the acetate base of the others. Coating defects, i.e., irregularities in the emulsion, have been observed in both makes and are, in their rare cases of occurrence, obvious mostly as stripes or streaks parallel to the film length.

It may be mentioned that in the first year after the war considerable quantities of Agfacolor perforated 35mm negative motion picture film were put on the market, illegally, in the form of special magazines. The sales agencies offered them as reversal film. The fact is mentioned here to point out that the gradation of color negative films is completely unsuitable for use as reversal film. Only by special processing methods can a less than mediocre transparency result be obtained with this negative material.

Processing Gevacolor Film

The processing of the Gevacolor Negative films, in principle, follows the formulae just given. Some deviations exist because, due to extra long rinses, the treatment requires more than twice the time. The color developer is very similar to the Agfa formula given above and differs mainly in its content of potassium bromide. The color developing agents can be changed. In any case it is possible to use p-amino-diethylaniline hydrochloride here too. It is important that the Gevacolor Negative film because of different gradation requires a longer developing time and a higher temperature than Agfa film.

A special developing agent, "Gevaminol," produced by the Gevaert company at one time, did not prove itself for the negative process because of fog formation but was well suited for the Gevacolor print paper. At the present time conversion to a new specially substituted compound, "Gevadiamin," is being carried out.

The hydroxylamine hydrochloride plays an important role in Gevaert's developer also. As alkali, sodium carbonate, is used in place of potassium carbonate. The long washing after the development in case of this negative material is substituted by a short rinse of 10 seconds. Then follows the stop bath which acts simultaneously as fixing and as hardening bath, contrary to the procedure of Agfa which works with a special hardening bath, but without stop bath. The long washing has been postponed to this point after the stop bath, and 30 minutes are considered necessary to avoid the color reaction with the bleach bath. This washing can be carried out in bright light. The bleach bath has a composition similar to the one above, but sodium acetate serves in this case as buffer.

The following rinse (10 minutes) is twice as long as in the Agfacolor Negative process. The subsequent fixing bath is alkaline and contains a small quantity of sodium sulfite which aids in stabilizing the formed dyes. After another rinse of 5 minutes, the stabilizing bath proper follows, which is not required for any of the other negative color film types. It consists of an alkaline formaldehyde solution. For Gevacolor the function of this bath is important. Only by the application of the solution mentioned can the decomposition of the yellow layer of the film be avoided

Processing Ferrania Film

The chemical composition of the color developing agent proper has not been defined by the manufacturer. This substance is furnished under the code name "S 41." The chemical properties indicate that it too is a derivative of p-aminodiethylaniline, possibly with a hydroxyl group as additional substituent. According to the exposure conditions of the film a liberal tolerance in the developing time is allowed. It is given as 7 minutes at 18C normally, but can be varied between 5 and 10 minutes, if tests prove adjustments to be necessary. These extreme variations are intended mainly for negatives on cine film, i.e., for the purposes of the motion picture industry.

The developer is followed by a rinse of 20 minutes. The directions do not consider a stop or hardening bath. The temperature of all later baths should be at about 15C unless specified otherwise in order to avoid damaging the gelatin. The subsequent bleach bath has the usual composition, potassium ferricyanide and potassium bromide, in a somewhat greater concentration than usual. Afterwards there is another rinse for 10 minutes.

Development of the Silver Mask

Now follows the special process which distinguishes Ferraniacolor and Telcolor from the two other makes; the development of the black-and-white mask. Because the silver has largely been converted to silver bromide by the preceding bleach bath, it regains in this manner its light-sensitivity. This fact can be used to generate a weak, negative, silver image in the film by a controlled exposure. A very soft-working Metol developer serves for its development. Suitably the film is exposed for about 5 minutes to a light intensity of about 100 foot-candles. Then the special Metol developer is employed until a density of 0.4-0.45 has been produced on the unexposed film edge. About 3 minutes developing time are required. The composition of a suitable Metol developer follows:

Metol	2 g
Sodium sulfite, anh.	20 g
Disodium phosphate, cryst.	30 g
Potassium bromide	1 g
Water to make	1 l

Thus only a part of the residual silver bromide is reduced with the mask developer, and it is important that the developed mask is neither too thin nor too dense. If the mask is too thin, it is ineffective, if too dense, it increases the printing time, shifts the gradation, and leads to halation phenomena. In the final print there occur shifts in the color tone in the dark color areas, e.g., redbrown instead of black. After completion of the mask development there follows a rinse for 5 minutes and then fixation for 5 minutes, using a neutral fixing bath, prior to the final rinse.

Processing Telcolor Film

The negative processing procedure of the firm of Tellko is closely related to the method of Ferrania. It is true that no details as to the composition of the baths have become known, but because the packaged chemicals must be separated in their containers due to their reactivity, conclusions can be drawn as to the quantities of the components. The firm of Tellko also recommends the mask method as the best possible development, but its instruction literature also describes a mask-less standard development, according to the principle of Agfa and Gevaert, because the technical manipulation is simple and the resulting reproduction satisfactory in many cases.

Again the standard developing time amounts to 7 minutes at 18C A rinse of 15 minutes is provided, no hardening or stop bath, and a bleach time of 5 minutes. The composition of the bleach bath resembles that of Ferrania. Exposure for 5 minutes with a light intensity of 100 foot-candles follows and development of the black-and-white mask with a density of 0.4 in 3¹/₂ minutes. Five minutes rinse, 5 minutes in the normal fixing bath, and the usual washing of 20 minutes complete the process. Table I shows the far-reaching parallelism of the various procedures and their differences in the treatment times.

Some remarks should be made on the light conditions during the processing. The development itself—or in the case of the mask process the first development—should suitably be carried out in complete darkness. If for one reason or another working without any illumination is not feasible, each manufacturer recommends a special darkroom filter. However, it has been established that a darkroom filter suitable for panchromatic materials of highest sensitivity may be used if the customary darkroom rules are observed. The same illumination is necessary for the following washing or all steps preceding the bleach bath. Only after the film has been treated for 2 minutes in the bleach can it be exposed to normal room light without damage (but preferably not to daylight because solarization phenomena may occur then).

The results obtainable with the four film types reveal a close similarity in their general character if mask development has not been carried out. Each emulsion type, regardless of the manufacturer, has its characteristic color tint, and it is not always possible to differentiate the various makes by a specific color tint, if they are submitted after development. However the spectral transparency of the formed dyes is very different in the individual makes so that an unfiltered test print during the printing technique (to be described later) reacts immediately with a strong shift when two identically appearing negatives of different manufacture are examined. Nevertheless the various film types can be printed on color papers of different origin provided that the correct required printing filters have been selected.

NOTE. The second part of Dr. Gordon's paper, dealing with European color positive materials and processes for making color prints from color negatives, will be published in the next (December) issue.
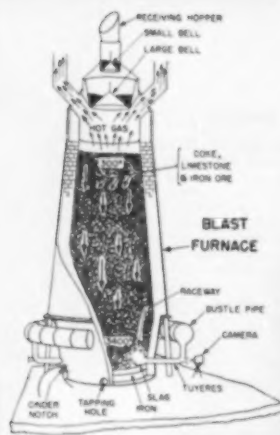
PHOTOGRAPHY IN STEEL RESEARCH

R. A. Buchanan*

Fig. 1.   Cut-away View of a
Modern Blast Furnace.

Fig. 2.   The modi-
fied 2 inch peepsight
(shown at the left) and
the normal ¼ inch
peepsight (shown at
the right).

As a research tool photography has become more
valuable with the introduction of the high speed motion
picture camera.   The particular camera we use is of the
rotating-prism type capable of speeds up to 3500 frames
per second.   This terminal speed has so far proved ade-
quate for practically all applications in the laboratory
and steel mills.   The greater part of our work is in
photographing self-luminous subjects.   In this cate-
gory we find welding electrodes, the combustion zones of
blast furnaces, open hearth tapping streams, and flame
studies.   There are, however, many subjects that must
be illuminated by artificial means.   Impact testing, oil
and water quenching, machining of steels, and piercing
of seamless tubing are but a few that may be mentioned.
One of the most fruitful applications of the high speed
camera in the steel industry, however, has been its use in
studying the blast furnace.   The blast furnace is the
most fundamental unit in a steel plant because it is
responsible for the reduction of iron ore to metallic iron.

The Blast Furnace

Although the blast furnace has been in use for many
hundreds of years, surprisingly little is known of the
processes taking place inside the unit.   This is largely
due to the nature of the furnace and its mode of operation.
A modern furnace (see Figure 1) consists essentially of a
suitably shaped, steel encased, brick tower about 80' to
100' high with an inside diameter of about 25' at the
bottom.   Into this tower some 2500 tons of iron ore,
1200 tons of coke and 500 tons of limestone are charged
daily and from the bottom liquid iron is withdrawn

about every 5 to 6 hours with a total yield of 1000 to
1500 tons per day.   The temperature varies from about
300 F at the top to some 3400 F at the bottom.   This
latter temperature corresponds to such a bright white
heat that the human eye can distinguish little in the
furnace without the aid of colored glasses.

In order to withstand these exacting conditions the
walls are made of special brick and are up to 3' thick
with many metal water coolers built in to increase the
life of critical areas.

It is not surprising, therefore, that there have been few
attempts to study the inside of the furnace during normal
operation, since it is obviously difficult to insert probes
and withdraw samples under these conditions.   The air
required to burn the coke is blown in, under a pressure of
15 to 20 pounds per square inch, near the bottom of the
furnace through some 15 to 18 blow pipes or tuyeres
which are steel tubes 8 feet long and 6 inches in diameter.
It has been found useful to equip these tuyeres with a
¼ inch sight-hole covered with a blue glass so that the
furnace operators can see along the tuyere and into the
bottom of the furnace (see Figure 2).   In this way
particles of coke can be seen moving at such high speed
that the eye has difficulty following them.   This rather
limited vision has been of great aid to the furnace oper-
ator and it seemed that a program of study, based on the
use of the high speed camera, might prove of value.

It is well known that the preheated air entering the
furnace burns the coke which is essentially the only
solid material at this point in the furnace.   The com-
bustion results in very high temperatures; 3400 F has
been reported.

Preparation for Photography

It was realized that the temperatures involved were
high enough so that the subject would be self-luminous
but that a special viewing arrangement or peepsight
would have to be designed.   This consisted essentially
of enlarging the viewing window from the normal
¼ inch to about a 2 inch diameter (see Figure 2).   This
opening was large enough to prevent interference with
the camera lens.   In the early design a pyrex glass was
used and an arrangement made to cool it by blowing
compressed air across the inner face since the temperature
of the air in the tuyere itself may be as high as 1000, or
even 1200 F.   It was found, however, that the cooling
air introduced halation effects and a 2 inch flat-ground
disc of fused silica was successfully substituted.   In this
way a view could be obtained of the combustion zone of
the furnace through a tube 6 inches in diameter and about
8 feet long (see Figure 3).   This gave an angle of vision
of about 3½°.   A four inch lens is used on the high
speed camera so as to magnify the 6 inch diameter image
as much as possible.   Kodachrome Type A film is being
used throughout the investigation.

Light Intensity Fluctuations

In the early work a great percentage of the films were either over or underexposed. It was difficult to understand why the exposures should vary so much, particularly since the same film, camera speed and diaphragm opening were used in each exposure. Assuming these factors to be constant, it became evident that the brightness was fluctuating considerably.

In order to determine how much the light intensity varied a regular photographic exposure meter was used to record the illumination in terms of foot candles. The meter was held in place in front of the two-inch glass opening and a number of readings were made over a period of one hour. The readings ranged from 25 to 250 foot-candles. In one instance, the light intensity changed from 140 to 250 foot-candles in less than one minute.

This simple experiment indicated that an exposure meter of some sort would be required for all future blast furnace work. A standard brand photoelectric cell meter was purchased and calibrated for high speed work. Since this meter has been adopted, virtually all films have been correctly exposed.

Results

When considering the outcome of these photographs it must be stated that they have led to a large and rapidly expanding program of research. Therefore, any detailed discussion is difficult and would probably be of more interest to students of metallurgy than to those whose primary interest is in photographic techniques. However, it is probably of interest to summarize the main results so far obtained. More detail is given in a report by Elliott, Buchanan and Wagstaff.[1]

Undoubtedly the most important results have been those obtained indirectly, that is, in answer to questions provided by the movies themselves. The observer looking at the pictures appears to be looking at particles
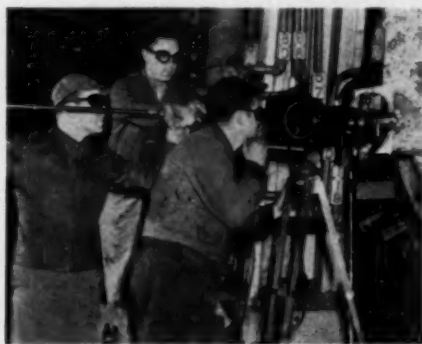

Fig. 3. The high speed camera in place to photograph the combustion zone of a blast furnace. The long rod shown in the photograph is part of a water-cooled probe used to determine the depth of the combustion zone.
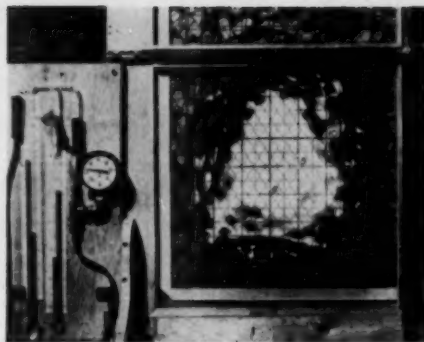
Fig. 4. A glass-sided model, representing a vertical cross-section of a blast furnace, demonstrates the circulating zone before a tuyere.

moving away from the camera at high speed. That posed two questions: what were the particles, and why were they moving at high speed at the bottom of an 80 ft. tower filled with granular solids?

The answer to the first question was obtained by photographing a furnace under unusual conditions when it was known to contain nothing but coke. It was found that the particles observed at that time were similar to the majority of those normally observed. It was therefore concluded that the majority of the particles in the normal furnace were coke, but that occasionally agglomerates, which were later found to be mixtures of slag, coke, and partially reduced ore, fell into this tuyere zone of the furnace. The movement of the particles was more difficult to explain. It was estimated from the film speed that the particles moved at speeds ranging from 20 to 200 ft/sec and the direction of motion suggested that recirculation of some sort occurred. To explain this a glass-sided model was built to simulate a vertical cross-section of the furnace through the tuyere (see Figure 4).

It is admitted that the model does not precisely represent the combustion zone of a furnace because it is two dimensional rather than three. In addition there is no actual combustion such as takes place in a furnace. There is, however, a great deal of similarity between the high speed pictures taken through the tuyere of a blast furnace and those taken of the model. This similarity makes it appear that circulation of coke about a sizable void must occur before the tuyeres in a blast furnace.

In order to study the thickness of the raceway, smaller models were built. While these studies are still in progress, it can be said that under many conditions the raceways in a blast furnace are approximately spherical. The possible overlap of adjacent raceways has not yet been settled. The direct observation on furnaces is limited at the moment by the fact that the camera has to look along an 8 foot pipe and can only see through an angle of $3^{1}/_{2}$.

Another and much more direct result of this photographic study was obtained by investigating the size of

the coke particles. It is well known that the operation of the furnace is influenced by the size of coke, but up to the present time investigations had to be limited to measurements on ingoing coke because the bottom of the furnace was at a temperature of 3400 F and some 20 lbs/sq. in. pressure. Withdrawing samples for measurement is unreliable because of the high probability that the lumps would break or burn.

However, having once photographed the lumps it is possible, in theory at least, to project the films on a suitable viewer and measure the lumps one by one. This technique is obviously tedious and in practice was also difficult. A suitable viewer was available with which, by good fortune, the projected image was about life size. Considerable difficulty was experienced because the majority of the particles were nearly at the same temperature and appeared almost identical in brightness and color. It was then difficult to distinguish the outline of any particle when viewing a particular frame. However, by moving the film backwards and forwards it is possible to estimate the size of the particles.

It is too early to give the results of this work, which is still proceeding, but it can be said at this early stage that size gradings can be obtained which are rather different from those expected. Further, the size gradings differ considerably from furnace to furnace.

While it has been stated that the blast furnace program has been the most fruitful application of the high speed camera in steel research there is another use that is worthy of mention here.

In the study of welding electrode characteristics the camera was instrumental in answering a number of questions. The high speed films revealed the number of short circuits or arc extinctions per second. The number of extinctions varied according to the type of electrode being used. It was possible to determine whether the metal transfer from electrode to plate was globular or spray, depending on what type of electrode was under study.

There is no problem of artificial illumination, the welding arc supplying all that is necessary. Daylight type Kodachrome has been used throughout the investigation. A four inch lens plus two 3+ portra attachments are used to produce as large an image of the electrode as possible. With such an optical arrangement the lens-to-subject distance is about five to six inches. The lens is protected from liquid metal spatter by a suitable glass shield. The exposure is determined by making a number of experimental test shots and varying the stop opening. The best exposure, for our work, is 3500 frames per second at f/22.

Artificial Illumination

Lighting is the major problem that confronts the high speed camerman. Workers in this field have utilized everything from #2 Photoflood lamps to huge aircraft searchlights in their efforts to find a suitable source of illumination for their particular type of work.[2] We have found two sources of illumination which are ideal for the type of work we are called upon to do. The first is the 750 Watt spot which is manufactured for the express purpose of illuminating high speed subjects. A number of these lamps used in banks or as individual sources of light will meet the lighting requirements for a good percentage of our work. The second is the Henry Lester continuous flash unit which has been described more fully in the literature[3] (see Figure 5). These units flash thirty four #31 flashbulbs in one second of time, producing about 3,000,000 lumens of light. With such tremendous light output, small stop openings may be used producing high speed motion pictures with great depth of field. These flash units are particularly well suited for steel mill problems because they are easily portable and require only a 110 volt line for operation.

Today, high speed motion picture photography is an especially important factor in its innumerable applications to arrested-motion analysis in steel research. There has been a tremendous variety of applications for this medium and more are developing each day. The importance of such visual studies can by no means be over-estimated. Research engineers have need for the accurate knowledge of the time, space and force relationships which occur between parts that move too fast for visual observation. The high speed camera is adequately serving this need.

Fig. 5. The continuous flash unit is being used here as the source of artificial illumination in the study of the machineability of a steel specimen.

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PHOTOGRAPHY IN ROCKET RESEARCH

H. M. Cobb*

THE WHITE SANDS Proving Ground in New Mexico was activated in 1945 as a base for testing the high altitude and long range missiles which were undergoing development under the auspices of the Department of Defense. The Ballistic Research Laboratories of the Ordnance Corps were assigned the responsibility for the design, development and operation of all instrumentation used to acquire flight data and such other experimental data as might be required by the missile development agencies. Because of the huge cost of the rocket development program and the many complexities of obtaining the required data, all available optical and electronic types of instruments were employed as a means of assuring the most complete and the most accurate information on each missile launched. The data obtained by optical and electronic instruments has been invaluable to the missile development engineers as well as to the flight test engineers.

During the early stages of missile development, detailed studies of flight performance during the launching phase was required. Ignition characteristics, booster performance, stability of the rocket at subsonic and at transonic speeds, effects of different types of launching mechanisms and the effects of meteorological conditions were among the many details studied. Photographic techniques were depended upon to a very large extent during that phase of the program. High speed motion pictures, spectrographic and photometric records showed minute changes in performance as the development engineers tested the missiles under constantly changing conditions.

Fixed motion picture cameras near the launcher were used to observe take-off or launching performance of the missiles. By means of triangulation from a set of two or more of these instruments appropriately placed with respect to the launcher, the position of the missile and the pitch and yaw angles at a given time could be determined with high accuracy. Spectrographs near the launcher produced data on combustion characteristics of various fuel mixtures and photometric measurements of the jet formation gave an indication of the efficiency of the motor. These observations are still necessary for missiles in the early stages of development.

Following the launching tests the flight performance observations were required, becoming more complicated as the final development stages were reached. Until late 1946 only trajectory data were available since the instruments in use up to that time were tracking theodolite cameras equipped with short focus optics. These instruments record on each frame the azimuth and elevation of the optical axis at the time of exposure as well as a small image of the missile. The position of the

Fig. 2. Photograph of A-4 missile, at a distance of 8 miles, taken with the 4.5 inch tracking telescope with 20 foot focal length. Portions of the 35mm frame not reproduced here contain azimuth, elevation and time records.

missile in the frame is measured to determine the tracking error. Thus the direction of the missile from the station may be determined. By synchronous observations from two or more stations the space position of the missile may be determined. Although theodolite camera observations do not give trajectory data with high accuracy they are capable of producing moderately accurate trajectory in a comparatively short time. Under normal atmospheric conditions observations may be obtained on a V2 missile to an altitude of approximately forty miles.

To meet the needs of more detailed observations at high altitude, Ballistic Research Laboratories initiated the development of long focus tracking instruments. The first instrument, built as an experimental model (Figure 1), consisted of a 4.5 inch refractor telescope of 60 inches focal length equipped with an amplifying lens near the prime focus to produce an effective focal length of approximately 20 feet. This optical system was mounted on an M45 machine gun turret which served as the tracking mechanism. A standard motion picture camera was used as the recording device. This instrument provided the first definite proof that the V2's were tumbling and spinning at high rates after burnout. This information led to improved flight control techniques by which considerably better missile performance was obtained. (Figure 2).

The successful performance of the 4.5 inch telescope dictated further development along this line. Two 10 inch Newtonian reflectors, a 16 inch Newtonian reflector (Figure 3) and a 10 inch Cassegrain reflector followed in order. Observations obtained by these instruments have given information regarding how missiles performed and often why they performed as they did. Functional failures, separation of booster rockets and ejection of experimental apparatus may be observed. Photometric and spectrographic studies of the jet flame at high altitudes and at high speeds have furnished information regarding fuel burning processes and heat distribution within the jet and have given an indication of aerodynamic flow patterns around the base of the missile. Orientation of the missile axis and rate of spin may be

* Ballistics Research Laboratories, Aberdeen Proving Grounds, Aberdeen, Maryland. Presented at the PSA National Convention, New York, N. Y., 13 August as part of the Technical Division Symposium on Photography in Engineering and Science. Received 25 July 1952.

69

determined from these photographic observations with a high degree of accuracy.

To meet the requirements for positional measurements of high precision, the Ballistic Research Laboratories have performed studies in photogrammetric techniques utilizing instruments patterned after the so called Ballistic Cameras developed during the early 1940's for use in bomb table observations. Consisting of a set of stationary plate cameras which are calibrated by means of stellar photographs, this system, under good conditions, is capable of giving angular measurements to a precision of about one part in one hundred thousand. Although the cameras in use at the present time are not properly designed for the requirements of the guided missiles program, they have provided the research data necessary to design an adequate photogrammetric instrument system. Such a system is presently being built.

One of the more recent problems imposed by the guided missile program is that of determining the nearest approach of a missile to a moving target at high altitude. This problem has been partially solved by a specially designed tracking telescope with a field of view large enough to cover the space around the target within which a missile would be considered as having scored a hit. Actual positions of the target and missile are not required. Hence the distance of the target from the instrument need be determined only with sufficient percentage accuracy to determine the scale of the photograph with a required accuracy. The instruments track the target and if a hit is scored the missile will appear on the photograph with the target. If the scale of the photograph is known to an accuracy of 1% then the actual distance between the target and missile may be determined to an accuracy of 1%.

Fig. 1. Twin 4.5 inch tracking telescope on modified M-45 machine gun mount, showing recording and tracking instruments. The effective focal length may be varied between 15 and 35 feet. Photographs on 35mm film are taken at rates up to 20 exposures per second.

Fig. 3. 16 inch tracking telescope on modified 90mm mount, of effective focal length from 40 to 80 feet. The instrument is located 40 miles from the launching site, at an elevation of 8000 feet.

To obtain these observations the Ballistic Research Laboratories designed and built a set of 16 inch reflectors of a modified Newtonian type. These telescopes are mounted on a modified 5 inch Navy Gun Mount and are equipped with cameras operating at 60 frames per second. Instruments are placed at stations at corners of a square so selected that the hit will occur over the approximate center of the square. Thus sufficient observational data is obtained to overcome any difficulties of reduction due to perspective.

Photographic observations have furnished a great deal of information which could have been obtained by no other instrumentation method. Malfunctions often destroy electronic units which are missile borne causing the loss of telemetry records. In addition certain details of performance can often be studied much more readily by means of photographic records than by other types of observations. Reduction of photographic records are, in general, slow and laborious. Meteorological conditions often make photographic observations impossible and the many problems involved in missile illumination, synchronization of camera operation, anomolous refraction of light waves, tracking mechanisms and mechanical construction of optical instrument mounts provide a field for continuous research and development.

DETERMINING CORRECT EXPOSURES FOR UNUSUAL INDUSTRIAL PHOTOGRAPHS USING A BRIGHTNESS METER

Tom Knowles*

IN 1941, Loyd A. Jones and H. R. Condit published a paper entitled, "The Brightness Scale of Exterior Scenes and the Computation of Correct Photographic Exposure." This paper gave a comprehensive treatment of the factors affecting the exposure of exterior scene photographs. The fundamental principles presented by Jones and Condit have been applied to other types of photography. The present author has applied his interpretation of these principles to commercial interior photography, particularly in the industrial field.

Many an industrial photographic subject has a range of brightness that makes correct exposure determination difficult, if not impossible, using conventional photoelectric exposure meters. Examples would be an inspection process in subdued light utilizing the fluorescence of materials under ultraviolet light or small, very bright detail of projected images. In some cases the exposure must be determined by evaluating from a distance the brightness of important small scene elements. Examples of these may be photographs taken through an inspection window of a laboratory testing chamber or a display sign mounted at an inaccessible height. In the method to be presented an attempt has been made to predetermine the negative densities that will result from exposure to the brightnesses of accurately measured scene elements. By producing negatives with the desired densities, the quality of the final prints will be assured with a minimum of special printing treatment.

A technically correct negative may be considered as one in which the brightness scale of a scene is represented by equally proportional steps of density in the negative. However, flare light adds an over-all density to the negative which may tend to veil the shadow detail. The broken portion of the curve SH, Figure 1, indicates the region most affected by the flare light. For all practical purposes the highlight density can be considered unaffected by flare which, nevertheless, makes it impossible for the scene brightness pattern to be exactly represented by equally proportional steps of density in the negative.

Another unavoidable factor which affects the image illumination in a manner not present in the scene is the reduced illumination off the lens axis. The writer found normal angle lenses (56°) to produce negatives having 86 per cent density at the corner compared with 100 per cent density at the center of the negative. Also, the wider the angle of a lens, the less the value of the off-axis illumination. A 90° wide-angle lens produced a density
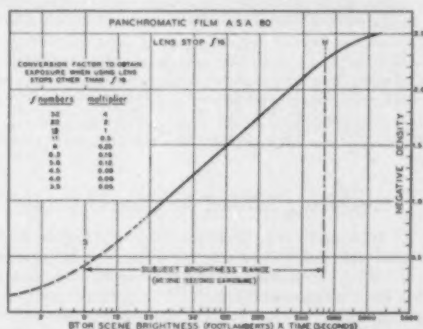

Fig. 1. Characteristic curve of Super XX film, statistically determined and plotted against time-intensity data for exposure determination. The lower scale B T represents scene-element brightness in foot-Lamberts multiplied by exposure time in seconds. B T is plotted against the resulting densities of a negative exposed in a camera at a lens stop of f/16 and developed to gamma 0.80. To obtain exposure time necessary to produce a desired density, divide the required B T by the brightness of the selected scene element. For lens stops other than f/16, use the conversion factor in table, Figure 1. Choosing exposures on the linear, S H, portion of the curve is not essential but will permit some additional tolerance allowance for unforeseen variables.

only 50 per cent at the corner of the negative as compared with 100 per cent at the center. The technical aspects of flare light and off-axis illumination has been completely covered by Jones and Condit.[2]

Keeping in mind the following probable variations: (1) the disturbing effect of flare and scattered light; (2) the problem of off-axis illumination reduction; (3) the variations to be encountered between successive settings of the same and different shutters and lens stops;

Fig. 2. Luckiesh-Taylor Brightness Meter.

(4) lens transmittance; (5) object to camera distances. Due to small variations in equipment, solutions and sensitive materials, it was decided that some factor of safety should be applied. The author choses to work with exposures as closely on the straight line portion of the D-log E curve as can conveniently be managed.

The method of exposure determination to be described is admittedly subject to some degree of error, due to the factors just described; nevertheless, it has much merit, particularly in the more difficult scenes. This method of exposure determination involves: (1) measuring the brightness of *critical subject elements;* (2) evaluating the characteristics of negative and printing materials; (3) correlating the range of brightness in the subject with the ranges of the negative and paper; (4) adjusting high brightness-contrasts in the scene, if possible, and; (5) computing the exposure for the desired rendition of the scene.

Measuring Subject Brightness Range

A Luckiesh-Taylor Brightness Meter (Figure 2) may be used for the measurement of subject brightnesses. This meter contains a battery-operated comparison lamp with a rheostat control. The optical system has a viewing angle of one degree. The important elements of the subject to be photographed can be viewed through the meter adjacent to a field illuminated by the comparison lamp. By rotating a continuous-density wedge, the selected scene brightnesses can be matched and measured. The primary range of the instrument is 2 to 50 foot-Lamberts, but this range is greatly extended by the built-in filters which can be inserted on either the scene or the comparison-lamp optical system. These filters extend the range from 0.002 to 50,000 foot-Lamberts. In practice, the brightness of white paper in full moonlight measures about 0.03 foot-Lambert; the brightness of fresh snow in direct sunlight measures from 5,000 to 10,000 foot-Lamberts.

The S.E.I. Exposure Meter (manufactured by the Salford Electrical Instruments Ltd., Manchester, England) serves substantially the same purpose.

Characteristics of Negative and Printing Materials

The film selected, to illustrate the principles discussed, was Super XX Panchromatic. This type of film

has a relatively long straight-line portion in its characteristic curve, Figure 1. This curve was obtained statistically from the sensitometric data obtained by the author. Eleven lenses varying in focal length from
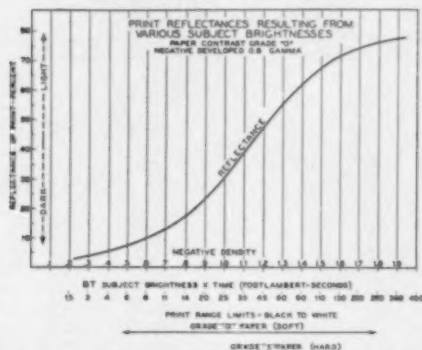
Fig. 3. Estimates of print values are read directly from "Subject-Brightness-Time" scale or the negative-density scale. The values and the relationship between the brightness-time and density are taken from Fig. 2. The curves are typical of those obtained from Azo F contrast grade O paper printed in contact with the negative. Printing exposure is 5 seconds at 70 foot-Lamberts printer brightness.
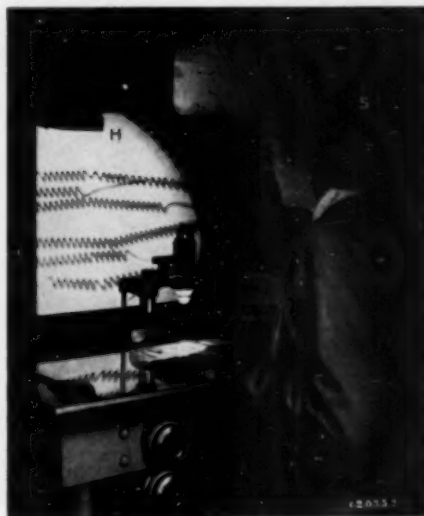
Fig. 5. The highlight area H measured about 10 foot-Lamberts. A floodlight was adjusted to retain some detail of the model, but did not illuminate the screen of the contour projector. The girl's hair was illuminated to 0.5 foot-Lambert or about $\frac{1}{20}$ of the screen brightness. The exposure given was 10 seconds at f/16.

72

Fig. 4. This nomogram type of "Exposure Calculator" is based on the brightness of a selected shadow area of the scene. A straight line is passed from the minimum-brightness scale on the left through the selected lens-stop in the center scale. The exposure time can be read from the right-hand scale. The resulting shadow density should be about 0.4 when the negative is developed to a gamma of 0.8.

$3^{1}/_{2}$ inches to 12 inches were used. The datum scene area was located 25 degrees off the axis of the lens in order to make some allowance f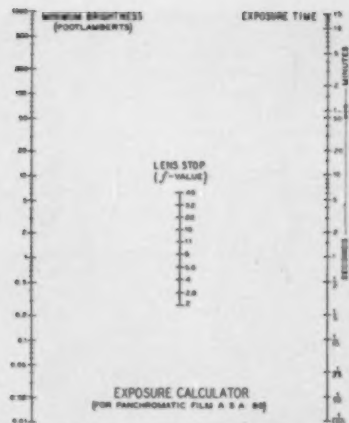or the reduced illumination at the corners of the negative. The camera lens was kept at a distance greater than fifteen times the focal length of the lens in order to avoid correcting for the bellows factor. The test surface was uniformly illuminated. The average scene may produce more flare light than the conditions under which these data were taken. This would tend to produce somewhat greater densities in the shadow area of the negative than is indicated by broken portion of the curve in Figure 1.

The printing paper used was Azo F glossy. The sensitometric response of this paper is presented in Figure 3.

Correlating Ranges of Scene, Negative and Paper

To determine the photographic exposure for a scene, brightness measurements must first be made of a few important subject elements. Portions of the scene that are to be rendered at the extremes of the print gray-scale, near-white, and near-black, are the critical areas. The measurements of brightness that are usually most essential are those of the critical areas to be reproduced as very dark gray or near-black in the final paper print. In some cases the highlight area is obviously the more important critical detail. Usually, the intermediate brightnesses will reproduce satisfactorily as gray tones.

The lower scale BT, Figure 1, represents the scene element brightness in foot-Lamberts multiplied by exposure time in seconds at a lens stop of f/16. For the sake of brevity the letters BT will represent brightness multiplied by exposure time. The curve SH, Figure 1, shows the relationship between the brightness of scene
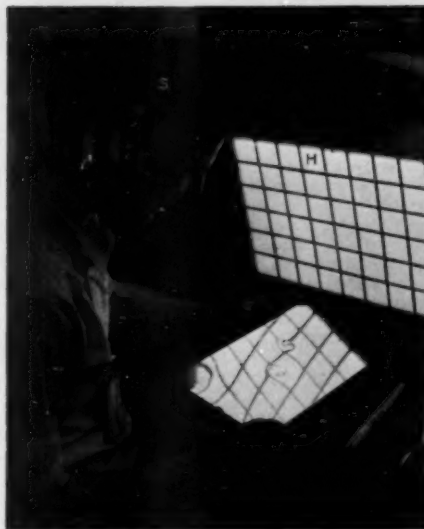

Fig. 6. The diffusing white glass H over the light source was the brightest part of the picture and measured about 200 foot-Lamberts. The hair of the worker S was considered the darkest scene element to be rendered. It measured 6 foot-Lamberts and was raised to 10 by means of a small floodlight. The ratio of shadow to highlight brightnesses was 1 to 20. The exposure was ½ second at f/16.

elements, exposure time, and negative densities. It is used as the basis of exposure calculation. A conversion-factor is used to obtain exposures for lens-stops other than f/16 (see Table, Figure 1). Assuming the exposure-time to be one second, then the scale reads directly in foot-Lamberts. Conversely, assuming the brightness to be one foot-Lambert, the scale would read in seconds.

For exposures other than unity (one second), divide the BT (foot-Lambert-seconds) required to produce a desired density by the foot-Lambert brightness of a selected portion of the scene. For close-up photographs, those made at a distance less than 10 times the focal length of the lens, some exposure correction must be made. A number of simple calculators are available that are based on the following formula:

$$\text{Effective f-value} = \frac{\text{Distance from lens to film} \times \text{rated f-value}}{\text{Rated focal length}}$$

For practical purposes, we can assume that the reciprocity law is effective over the range of exposures usually encountered. Over this range the same negative density will result from any combination of subject-brightness multiplied by exposure-time, the product of which is constant. For example, 1 second at 100 foot-Lamberts, 10 seconds at 10 foot-Lamberts, 100 seconds* at 1 foot-Lambert, produce approximately the same density.

* Beyond these values correction must be made for reciprocity failures.

For the purpose of illustration, assume that the brightness of the critical shadow area, S, of a scene is 5 foot-Lamberts and the critical highlight area, H, is 800 foot-Lamberts. This shadow-highlight brightness ratio of 5 to 800 is approaching the limit of the straight-line portion of the curve at the points S and H, respectively, Figure 1. The densities produced by 5 and 800 foot-Lambert-seconds at stop f/16 would be 0.4 and 2.24, respectively, Figure 1. Exposures appreciably below and above these values will not produce negative densities in proportion to the brightnesses of the corresponding scene elements. From a subjective viewpoint many fine photographs are made by utilizing the non-linear portions of the negative curve, particularly the toe. It is usually safer to place the exposure for the minimum scene-brightness on the straight-line portion of the curve at about the point S, Figure 1. Using modern emulsions of the type used in this presentation there is little danger of over-exposure. This is due to the great scene-brightness range, about 500 or 1000 to one, that can be recorded by these negative materials.

The dark-to-light range of the negative is substantially greater than that which can be reproduced by even the softest-contrast grade O printing paper. The linear response of the negative material is approximately 1 to 160. The range of scene-brightnesses reproduced by low contrast grade O paper is only about 1 to 40. The scene range of high-contrast grade 5 paper is only 4 to 1, Figure 3. The density scale of the negative and the subjective choice of the photographer will determine the most desirable printing-paper contrast.

The reflectance curve in Figure 3 indicates the gray values of a print made on grade O paper, exposed through a negative-density range, and the corresponding subject element exposures (BT) that produced them with a lens-stop of f/16. In the example mentioned, with a negative-density range of 0.4 to 2.24, the resulting print reflectances will be 7 per cent (near-black) and 78 per cent (near-white), respectively. (See Figure 3.) This print will lack shadow and highlight details. If no critical details existed in either the shadow or highlight area, the print may be quite acceptable.

The limits of the reflectance range of white, glossy printing paper (regardless of contrast grade) are about 4 per cent and 78 per cent. This is a reflectance brightness-ratio of about 1 to 20.

If it is desirable to reproduce the brightness-range of the original scene in a glossy paper print, the scene brightness-range should not exceed 1 to 25. Subject elements in which no detail is to be retained obviously may have brightnesses outside of the 1 to 25 range. The resulting negative should print on an #1 or #2 contrast paper.

Adjusting Brightness-Range of Scene

The brightness-range of an industrial inspection bench may be so great that either under-exposure of the low tones or over-exposure of the highlights is unavoidable. If the brightnesses are known, or measurable, an excessive brightness-range may be reduced with supplementary floodlighting.

Assuming the brightnesses of the critical elements of a scene range from 1 to 100, this is about $2^1/_2$ times the printing range of zero contrast glossy printing paper. This high-ratio scene can be recorded on the negative, but printing the highlight and the shadow details calls for negative staining or print dodging, etc.

This special printing may be minimized by adjusting the light range of the scene to match a desired contrast printing paper. Obviously many night-time scenes such as lighted streets and other large illuminated outdoor areas must be photographed as they exist, regardless of the contrast range. These scenes are usually printed on very soft contrast papers. To obtain a negative for printing on number 1 or 2 contrast paper, the scene brightness range must be reduced to about 1 to 25. This is done by diffuse floodlighting to raise the brightness of the shadow area to about 4 foot-Lamberts. Where possible, reducing the brightness of the highlight area to 25 foot-Lamberts will have the same effect. In cases where the highlight brightness is produced by a source that can be turned off, such as a lighting fixture, it could be lighted only long enough to produce a brightness-time ratio not exceeding 25 times that of the shadow area.

Fig. 7. Brightness readings were made from the camera position directly through the window of this air conditioned test chamber. The selected highlight area H measured 10 foot-Lamberts. The shadow area S measured 0.75 foot-Lambert. The brightness of the lighting fixture was 900 foot-Lamberts. Detail of the fixture was considered non-essential and it was allowed to go off scale and record as white. The shadow-highlight ratio was considered to be 1 to 13. The exposure given was 7 seconds at f/16.
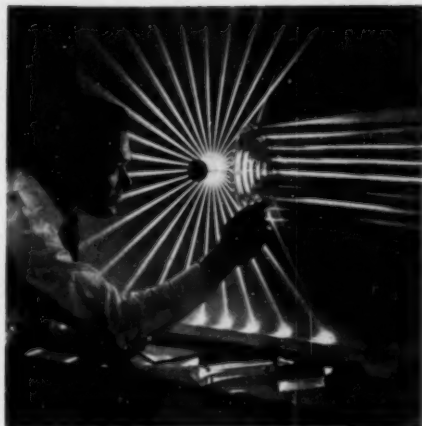
Fig. 8. The brightness of the radial pencils of light measured 5 to 10 foot-Lamberts. The dark area of the model's face measured 0.5 foot-Lambert and was considered the critical shadow area. Exposure – 5 seconds, F/11.

Computing Exposure

The exposure-time can be based on brightness measurements of either the shadow or highlight area. This provides the important product of brightness × time, or BT. The BT, for both the shadow and highlight areas should preferably fall on the straight-line portion of the curve between the points S and H, Figure 1. A typical indoor scene to be photographed could have a shadow brightness of 1 foot-Lambert and a highlight brightness of 25 foot-Lamberts. To determine the exposure for this scene, place the 1 to 25 subject brightness-range on the linear portion of the curve with 1 foot-Lambert at the point S, Figure 1. The scale, BT, for the subject will read 5 BT for the shadow area and 125 BT for the highlight area. The exposure in seconds is computed by dividing BT (to produce the desired density) by the brightness of the scene elements. Computing the exposure-time for the shadow area, 5 BT divided by 1 foot-Lambert (brightness) equals 5 seconds exposure. Based on the highlight area, the same exposure would result from 125 BT divided by 25 foot-Lamberts (brightness) or 5 seconds exposure. This exposure is based on a lens stop of f/16. The table in Figure 1 gives conversion-factors for lens-stops other than f/16. The negative is developed to a gamma of 0.8.

To simplify the determination of exposure-time, the nomogram, Figure 4, may be used. This calculator is based on the brightness of the critical shadow detail of a scene being photographed. The exposure is read from the right-hand scale when a straight line is passed through the minimum critical scene-brightness on the left and the selected lens-aperture in the middle. The exposure as read from the right-hand should give a density of about 0.4 for the critical shadow area.

Industrial Photographs

The photographs, Figures 5 to 8, inclusive, illustrate a few examples of industrial photographs made in accordance with the fundamental principles presented, which apply to many other types of photography.

Photographic equipment and processes have many variables affecting correct exposure. Fresh chemical solutions for processing, controlled development agitation, time, and temperature, must not be ignored if the final results are to be uniform.

Summary

Summarizing the steps necessary to determine the exposure of unusual scenes by the method described above:

1. Measure brightness of the darkest shadow and of the highlight in which detail is to be recorded.
2. Know the sensitometric characteristics of the negative and paper to be used.
3. Choose the desired negative densities on the straight-line portion of the curve SH, Fig. 1.
4. If the range of BT (brightness × time) exceeds 1 to 25, it may be reduced by:
 (a) diffusely floodlighting the shadow-area;
 (b) reducing the brightness, exposure, or both, of the highlight area, or
 (c) a combination of (a) and (b).
5. Determine the exposure-time by:
 (a) selecting the desired negative density on the curve, Figure 1. Then divide the required BT by the selected scene-brightness as measured with the brightness-meter. For lens-stops other than f/16 use the conversion table, Figure 1, or
 (b) read exposure-time from calculator (Figure 4) for any selected lens f-value. This method is based on the brightness of the critical shadow area as measured with the brightness-meter.

 Of course, some further computation may be necessary in terms of the photographer's own equipment, experience, and needs. When all of these variables have been taken into consideration this system of determining exposures will reduce the needless waste of time and materials caused by taking unnecessary trial exposures. Time will also be saved by knowing how best to adjust the lighting to produce negatives of predetermined density-range and desired quality. It also assures the operator of obtaining the best prints possible for any given set of brightness conditions.

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Kinetics of Development of Liquid Photographic Emulsions
II.   Development by Hydroquinone*

L. J. Fortmiller and T. H. James

ABSTRACT

The kinetics of development by hydroquinone of a dispersion of silver halide grains in dilute gelatin solutions were investigated over the pH range of 9–13. The development curve shows a marked induction period. The rate of development is expressed in terms of (1) the reciprocal of the time required to complete 5 or 10 percent of the reaction, and (2) the maximum slope of the density-time of development curve. The rate of development decreases to a minimum as the sulfite-ion concentration increases. The rate is proportional to the concentration of hydroquinone. The pH-dependence of the reaction indicates that the bivalent ion is the effective developing agent in the later stages of the reaction, but the univalent ion may play some part in development in the induction-period region. At high pH, the rate of development does not increase as rapidly as anticipated from its behavior in the lower pH region, probably because of an increase in the charge barrier surrounding the grains resulting from adsorption of hydroxyl ions. The apparent energy of activation is approximately constant over the pH range of 9.3–12.9 when correction is made for the heats of ionization. The activation energy calculated from the time required to complete 5 percent and 10 percent of the reaction is approximately 5 kcal/mole; that calculated from the slope rates is 8 kcal/mole. The activation energy of fog formation calculated from the time required to complete 5 percent and 10 percent of the reaction is 12 kcal/mole; that calculated from the slope rates is 21.5 kcal/mole. The addition of lauryl pyridinium p-toluene sulfonate to the developer markedly increases the rate of development, and quinone catalysis persists in the presence of the quaternary salt.

I N A PREVIOUS publication,[1] a method was described for investigating the kinetics of development of dispersions of silver halide grains in dilute gelatin solutions. This method avoids the complications often introduced by diffusion effects in the development of coated emulsions, and is particularly useful as a means of determining the apparent energy of activation of development. The present paper deals with the application of this method to the study of development by hydroquinone in the presence of sulfite.
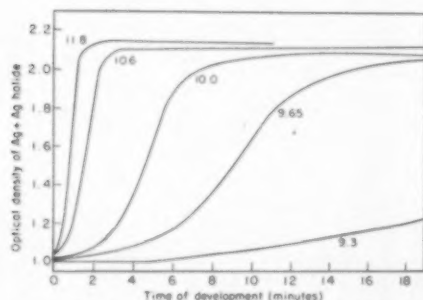

Fig. 1. Development of liquid emulsion by hydroquinone at the average pH levels indicated.

Experimental Procedure

The apparatus and general procedure followed in this work are the same as described in the previous paper.[1] Emulsion *B* (previous paper) was employed in preparing

the samples for all o the present tests. In most of the experiments, 90 grams of stock emulsion solution were added to 260 ml of 0.5 percent gelatin solution for each test, and the total reaction solution was made up to 500 ml. All solutions not containing gelatin were deaerated with High Purity Linde nitrogen before adding sulfite or hydroquinone. Nitrogen was kept over the reaction mixture during development. All rate measurements are for 20 C unless otherwise specified.

Experimental Results

The reaction curves in development by derivatives of p-phenylenediamine followed the first-order law over the major part of the reaction course. Development by hydroquinone, on the other hand, exhibits a marked induction period, during which the rate of reaction is

Table I

DEPENDENCE OF DEVELOPMENT RATE UPON HYDROQUINONE CONCENTRATION

Hydroquinone in Grams per 500 ml	Slope Rate	Time Rate for Partial Development			pH	Na₂SO₃ in Grams per 500 ml
		5%	10%	50%		
0.4	0.016	0.0016	0.0010	0.00036		
0.8	.033	.0033	.0019	.00068		
1.6	.067	.0059	.0040	.0014	9.5	0.40
3.2	.122	.014	.0083	.0029		
0.4	.019	.0012	.00090	.00045		
0.8	.041	.0018	.0013	.00082		
1.6	.079	.0033	.0023	.0013	9.5	3.9
3.2	.173	.0073	.0049	.0027		
0.4	.0073	.012	.0080	.0038		
0.8	.018	.024	.018	.0088		
1.6	.039	.059	.044	.020	11.0*	3.9
3.2	.070	.083	.067	.042		

* Emulsion used contained less AgBr than in preceding runs.
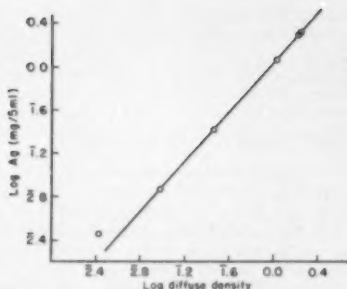
Fig. 2. Relation between developed silver and density.

Fig. 3. Dependence of rate of development upon sulfite content. ○ ○, 1/t rates for 5% development; △ △, 1/t rates for 10% development; x x, slope rates.

increasing with increasing time. Typical reaction curves are shown in Figure 1, where the optical density of silver plus silver halide is plotted against the time of reaction at various pH values. Satisfactory "first-order constants" cannot be obtained from such curves. Instead, the rates of development have been expressed in terms of (1) the maximum slope of the reaction curve in terms of ΔD per second (slope-base rates), and (2) the reciprocal of the time in seconds required to complete 5 percent and 10 percent of the total reaction (time-base rates).

The relation between the mass of silver formed during the course of the reaction and the diffuse density of the silver is given in Figure 2 for one experiment. The slope of the log-log curve is about 1.15. This indicates[2] that both the size and the number of silver particles increase as the reaction proceeds, so that the measured rates are a composite of the rates of initiation of development of individual grains and the rates of propagation of development through the grains.

The effect of sodium sulfite upon the rate of development is illustrated in Figure 3. The rate is at a maximum in the absence of sulfite, and decreases rapidly with increasing concentration of sulfite at first. The maximum effect of sulfite, however, is exerted at a concentration of one gram per liter, and not much change in development rate is produced by addition of sulfite in excess of about three grams per liter. Most of the subsequent experiments were carried out with 3.9 grams of sodium sulfite per 500 ml of solution, where the reaction rate is at about the minimum and the sulfite is in sufficient excess to give a comfortable safety factor.

The rate of development is proportional to the concentration of the hydroquinone. This is illustrated in Figure 4 for runs made at pH 9.45 and at two sulfite concentrations. Table I gives numerical results for these runs, together with results for tests made at pH 11.0.

The effect of pH upon the rate of development is illustrated by the curves in Figure 1. The pH values given are "average" values, since some change in pH occurred during the course of each reaction. The average values are the averages of the initial pH, determined by measuring the pH of the mixture omitting the stock emulsion, and the final pH determined after reaction is complete. The difference between the initial and final pH values generally amounted to approximately 0.1 pH unit. The pH-dependence of the slope rates and the reciprocal time rates are the same for pH values over 10.0.
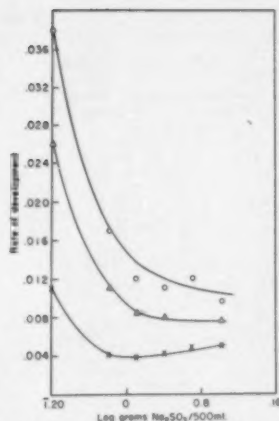
Below 10, the reciprocal time rates are somewhat less sensitive to change in pH. The D_{max} obtained for complete development decreases somewhat with decreasing pH. To compensate for this, all slope rates were corrected on a proportional basis to represent a D_{max} of 2.00.

In Figure 5, both rates are plotted as a function of pH, and are compared with the concentrations of the singly and doubly ionized hydroquinone present in the solution. These concentrations, plotted as Curves b and c were calculated on the basis of the following dissociation constants[3,4] for hydroquinone: $pK_1 = 10.0$, $pK_2 = 11.8$. Ten percent of the hydroquinone is in the singly ionized form at pH 9.0. This increases to a maximum at pH 10.8 and thereafter decreases because of the increase in degree of double ionization. Only one ten-thousandth of the hydroquinone is doubly ionized at pH 9.0, but one-

Fig. 4. Dependence of development rate upon concentration of hydroquinone at pH 9.45. ○ ○, 3.9 g. Na₂SO₃ per run; x x, 0.4 g Na₂SO₃ per run.

Table II

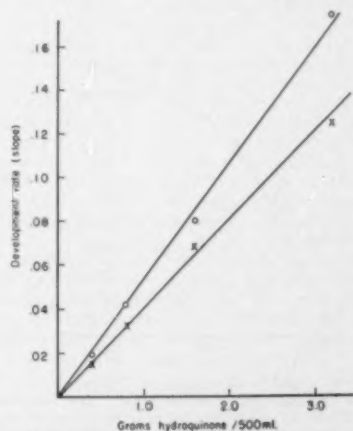| pH	Temperature Coefficient		Apparent Activation Energy in Kcal/Mole		Apparent Activation Energy Corrected for Heat of Ionization in Kcal/Mole		Method of Measuring the Rate of Development and Type of Test
	Uncorrected for ΔD	Corrected for $\Delta D = 1.0$ (slope rates only)	Uncorrected for ΔD	Corrected for $\Delta D = 1.0$	Uncorrected for ΔD	Corrected for $\Delta D = 1.0$	
9.3	3.10	3.02	19.3	18.9	8.9	8.5	Slope
11.0	2.46	2.30	15.4	14.3	9.9	8.8	rates.
12.9	1.82	1.59	10.3	8.0	9.7	7.4	Exposed emulsion.
9.3	2.65		16.6		6.2		Time rates
11.0	1.78		9.9		4.4		for 5% of development.
12.9	1.38		5.5		4.9		Exposed emulsion.
9.3	2.35		14.6		4.2		Time rates
11.0	1.88		10.8		5.3		for 10% of development.
12.9	1.34		4.8		4.2		Exposed emulsion.
12.9	3.72	3.64	22.5	22.1	21.9	21.5	Slope rate. Unexposed emulsion
12.9	2.12		12.8		12.2		Time based for 5 and 10%. or "fog."

tenth is doubly ionized at pH 11.0, and ionization is nearly complete at pH 13.

A single line is drawn through the development rates above pH 10.0 which are plotted in Figure 5. Below this pH, the curves for the slope rates and reciprocal time rates may diverge. The slope rates are proportional to the concentration of doubly ionized hydroquinone below pH 10, and hence the relative rates can be made to coincide with Curve *b* in Figure 5 by multiplying them by a suitable factor. The reciprocal time rates fall on a curve (bro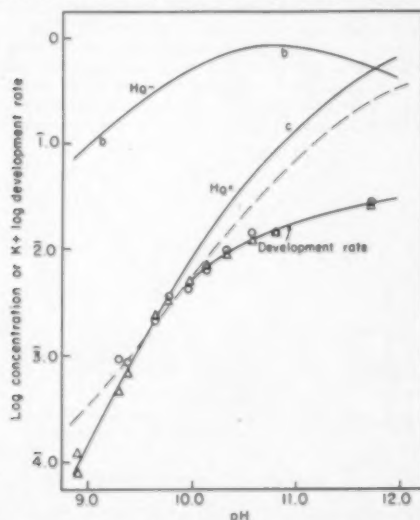ken curve) calculated on the assumption that singly ionized hydroquinone can act as a developer, but that the doubly ionized hydroquinone is 188 times more effective. Above pH 10, the rate of development is smaller than that predicted by Curve *b* or by the broken curve. This can be explained on the basis of the charge-barrier effect, as will be shown in the discussion.

The effect of temperature upon the rate of development by hydroquinone was measured over a temperature range of 12–34 C, and at pH values of 9.3, 11.0, and 12.9. The experimental data are given in Figure 6 and in Table II. As indicated by the figure, the maximum density obtained decreases somewhat with decreasing temperature. To compensate for this, the slope rates were corrected on a proportionality basis, as indicated in Table II.

The apparent activation energies were determined from an Arrhenius plot of log rate vs reciprocal of the absolute temperature (see Figure 6). The uncorrected values determined from the slope rates are 19.3, 15.4, and 10.3 kcal/mole for pH 9.3, 11.0, and 12.9, respectively. When these values are corrected on the basis of equal total change in density, they become 18.9, 14.3, and 8.0 kcal/mole. These values, however, are complicated by the heats of ionization of the hydroquinone. The degree of ionization of hydroquinone increases with increasing temperature, and Baxendale, Hardy, and Sutcliffe[a] give the heats of dissociation for the first and second ionizations as 5.3 ± 0.8 and 5.9 ± 0.5 kcal/mole. Using these values, and assuming that the divalent ion is the active species in development, we obtain the following corrected values: 8.5, 8.8, and 7.4 kcal/mole for pH 9.3, 11.0, and 12.9, respectively. The corrected apparent activation energy, thus, is essentially independent of pH. The activation energies calculated from the reciprocal time rates are lower than the values obtained from the slope rates, and average about 5 kcal/mole (see Table II).

The temperature-dependence of fog formation by the hydroquinone developer was determined at pH 12.9 over the same range of temperatures. The temperature coefficients and apparent activation energies are listed in Table II. These activation energies (22 kcal/mole for

Fig. 5. Rate of development compared with the degree of ionization of hydroquinone as a function of pH. Curve b, singly ionized hydroquinone; Curve c, doubly ionized hydroquinone; △ △, slope rates; ○ ○, reciprocal time rates for 10% development; - - - -, curve calculated for doubly ionized hydroquinone 188 times as effective as singly ionized hydroquinone.

the slope rates, 12–13 for the reciprocal time rates) are much higher than the activation energies calculated for image development.

The quaternary salt, lauryl pyridinium *p*-toluenesulfonate, markedly accelerates development of the liquid emulsion by hydroquinone. This is illustrated in Figure 7. The magnitude of the effect is so great that reliable rate measurements could not be made in the presence of the quaternary salt above a pH of 9.0 with the present equipment. The maximum density obtained in the presence of the quaternary salt was greater than than obtained in its absence, and analysis showed that the increase in density was accompanied by an increase in reduced silver. Some experiments carried out at pH 8.8 showed that sulfite still exerts a marked retarding effect upon the rate of development in the presence of the quaternary salt. For example, the addition of 3.9 grams of sulfite per 500 ml of reaction mixture increased the time required to complete 10 percent of the reaction in the presence of 0.001 *M* quaternary salt from 2 seconds to 10 seconds; it increased the time required to complete 50 percent of the reaction from 5 seconds to 22 seconds.

Discussion of Results

In comparing the results obtained in the present work with those previously obtained with coated film, certain differences are apparent. In the previous work with coated film,[2,5] the exposures were well on the shoulder of the characteristic curve, nearly all of the grains were developable, and the dependence of the photometric equivalent upon the extent of development indicated that the measured rates of development were primarily those of development of the individual grains. This interpretation was supported by the results of microscopic examination of the grains at various stages of development, and by the effect of partial predevelopment upon the bromide-ion sensitivity of the developer. In the present work, the dependence of the photometric equivalent upon the degree of development is much smaller, indicating that the measured rates are much more dependent upon the rate of initiation of development of the individual grains. The fact that the photometric equivalent is not constant shows that some increase in average particle size is occurring as development progresses. The measured rates in the liquid emulsions thus are dependent both upon the rate of initiation of development of the individual grains and the rate of continuation of development of those grains, a situation comparable to that previously found in the development of the toe and lower straight-line portion of the characteristic curve of the coated emulsions. In the present work, the calculated reciprocal time rates may correspond very closely to the rates of initiation of development of the most readily developable individual grains.

The importance of the charge effect in determining the measured rate of development of the liquid emulsions is shown by the marked acceleration obtained by adding the quaternary salt. It proved impossible to obtain reliable kinetic measurements in the presence of the quaternary salt at pH above 9 with the present apparatus because of the limitations imposed by the rate of mixing of the sample. It is noteworthy that at pH 8.8 the addition of the quaternary salt does not eliminate quinone
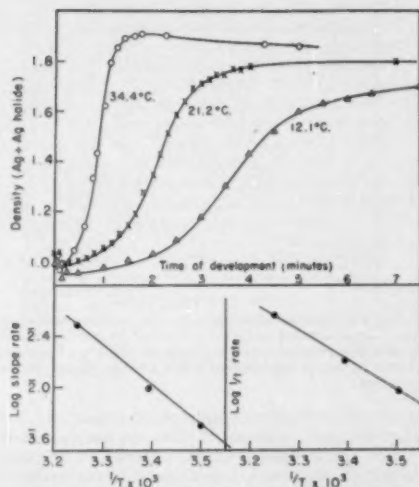

Fig. 6. Upper part: density vs time of development curves at temperatures specified, pH 11.0. Lower part: Arrhenius plots of data derived from upper curves.

catalysis, and this suggests that something more than the charge effect is involved in this catalysis.

The dependence of the slope rates upon the pH over the pH range, 8.9–9.8, can be accounted for satisfactorily on the assumption that the bivalent ion of the hydroquinone is the active developing agent. The dependence of the reciprocal time rates suggests that the univalent ion plays some part in the induction-period region, but the specific rate of development by the bivalent ion is still much larger. The charge effect[5] might be expected to greatly favor the univalent ion over the bivalent ion in the initiation of development of the individual grains and, hence, the univalent ion would take a relatively more prominent part in determining the reciprocal time rates than in determining the slope rates.

The fact that the measured rates cannot be accounted for quantitatively over the entire pH range by any assumed linear combination of univalent and bivalent ion rates suggests that some additional factor is involved. The measured rate at pH 12.0 is only about one tenth that calculated by extrapolation of the rates measured in the pH range, 8.9–9.8, as shown in Figure 5. A qualitative explanation of this discrepancy can be given on the basis of the charge effect. At pH 12.0 and above, the concentration of bivalent ion exceeds that of univalent ion and charge effects will be particularly important in determining the over-all rate. At the lower pH values, the charge on the grain surface is determined primarily by the bromide ion in the absence of modifiers such as the quaternary ions. At high pH, however, adsorption of hydroxyl ion may contribute a significant amount to the net charge. Chromatographic experiments carried out by Vanselow and James[6] show that hydroxyl ion at concentrations as low as 0.001 *M* (pH about 11.0) displaces the merocyanine dye, 4-[(3-ethyl-2(3*H*)-benzothiazolylidene)ethylidene]-3-methyl-1-(*p*-sulfophenyl)-
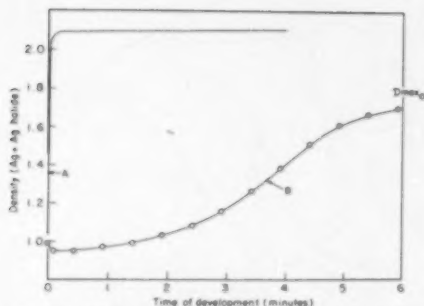
Fig. 7. Effect of lauryl pyridinium *p*-toluenesulfonate upon development of liquid emulsion by hydroquinone in the presence of sodium sulfite at pH 11. Curve A, 0.001 *M* lauryl pyridinium parts added; Curve B, no addition.

5-pyrazolone, from the silver bromide surface and, hence, is adsorbed to a significant extent. As the hydroxyl-ion concentration increases from pH 11.0 to 13.0, the amount adsorbed increases and, hence, the rate of development should be depressed to an increasing extent.

The dependence of the temperature coefficient of development upon the pH of the solution is that to be expected if the specific rate of development by the bivalent ion is much greater than that by the univalent ion. When the apparent activation energies calculated from the temperature coefficients are corrected for the heats of ionization of the bivalent form, the resulting apparent activation energies are essentially independent of pH. The corrected values for the reciprocal time rates vary between 4.2 and 6.2 kcal/mole with an average of 4.9, and can be considered constant within the limits of experimental error. This is roughly the activation energy

expected for a diffusion-controlled process. It may be postulated that the rate-controlling step in the initiation of development of the exposed silver halide grains under the conditions employed is the diffusion of the developer ions through the electric double layer surrounding the grains. The first-order dependence of rate upon concentration and the marked acceleration produced by the quaternary salt are entirely consistent with this postulate. It is possible, however, that the value 4.9 represents the apparent activation energy of the chemical reaction in which the catalytic action of the latent image is most efficient. The apparent activation energy calculated from the slope rates is 7.4–8.8 kcal/mole, which is high for a diffusion-controlled process, and probably represents the activation energy required for the development of grains which have smaller or less accessible latent-image centers than the ones represented by the first 5–10 percent of the course of development.

The activation energy calculated for the fogging reaction (reduction of unexposed grains) is 12 kcal/mole for the first 5–10 percent. The value calculated from the slope rates is much higher, i.e., 21.5 kcal/mole. Thus, it appears that the reduction of the most easily fogged grains has a considerably lower energy of activation than the reduction of the grains represented by the later portions of the reaction curve. The "more easily fogged" grains may be those with relatively large sensitivity centers.

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REDUCTONE AS A PHOTOGRAPHIC DEVELOPER

Olus J. Stewart*

Euler and Martius[1] isolated glucoreductone in 1933 and established its empirical formula, $C_5H_4O_5$. They noted its high reducing power, particularly in acid solution. Since no carboxyl group was present, Euler attributed the strongly acidic character to an enolic configuration and assigned the constitutional formula, $HO - CH = COH - CHO$. In view of the discoveries that both Vitamin C (ascorbic acid)[2] and Isovitamin C[3] are developers, it now is not surprising to learn that reductone, a closely related compound, also has developing properties. The ability of reductone to develop latent images was still more to be expected after Stenger[4] pointed out that reductone, a readily oxidized compound, should be able to develop exposed sensitive

material because its atomic configuration conformed to the newly formulated developer rule. About the same time the Wilmanns and Schneider[5] invention proposed to use developers which contained in their molecules the atom grouping $- CO - CHOH -$ or its tautomeric form $- COH = COH -$. However, reductone was not among the developers mentioned.

In order to prepare a reductone developer it is necessary, pending the establishment of a commercial supply, to synthesize the compound by the method of Euler and Martius, for example, or a modification thereof. Thus one may (a) prepare the chemical and use the purified crystals in the developer formula, or (b) after synthesizing the compound, omit the separation and purification processes, and simply employ the crude reaction mixture in the developer. Both of these procedures will appear in the following developer formulas.

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Reductone developers can be formulated to exhibit the unique property of yielding directly, without toning, warm tone, brown or even reddish prints. Perhaps the most practical way to describe these reductone prints in words is to compare them with the well-known warm tone prints which result directly when Kodak Athena paper is developed with Kodak Developer D-52. This project is here put into effect by presenting examples which, together with pertinent data, follow each reductone developer formula. It should be stated also that in preparing these examples, all photographic papers used were exposed through the same negative, and in the same contact printer.

REDUCTONE DEVELOPER R-1 FOR PAPERS

Water, about 50C	800.0 ml
Sodium carbonate, monohydrate	27.0 grams
Sodium hydroxide	6.8 grams
Sodium sulfite, desiccated	15.0 grams
Reductone, crystals	1.0 gram
Potassium bromide	4.0 grams
Water to make	1.0 liter

Example 6. Exposed Kodak Azo E 15 seconds; developed 10 minutes with Reductone Developer R-1 (1:2 water, 20C). The paper stock remained white; the image was brownish and more warm toned than Example 69.

Example 59. Exposed Kodak Athena 15 seconds; developed 20 minutes with Reductone Developer R-1 (1:1, about 20C). The face of the paper stock was slightly tinted, and the image was more warm toned than Example 69.

Example 69. Exposed Kodak Athena 15 seconds; developed 2 minutes with Kodak Developer D-52 (1:1, 20C). The print was warm toned, and the paper stock was slightly tinted.

REDUCTONE DEVELOPER R-2 FOR PAPERS

Reductone Developer R-1	1.0 liter
Hydroquinone	2.0 grams

Example 60. Exposed Kodak Azo E 10 seconds; developed 1 minute with Reductone Developer R-2 (20C). The print was not so warm toned as Example 62.

Example 62. Exposed Kodak Athena 10 seconds; developed 4 minutes with Reductone Developer R-2 (20C). The print was not so warm toned as Example 69, and the paper stock was slightly tinted.

REDUCTONE DEVELOPER R-3 FOR PAPERS
Solution A

Water (about 50C)	300.0 ml
Sodium carbonate, monohydrate	26.0 grams
Dextrose	50.0 grams

Heat 2.5 minutes at 91–93C. Cool quickly.

Solution B

Water (about 50C)	400.0 ml
Sodium sulfite, desiccated	45.0 grams
Hydroquinone	12.0 grams
Potassium bromide	4.0 grams

Cool, mix with Solution A and dilute to 1 liter.

When alkali and dextrose are mixed at 91°, a rise of temperature will be observed, indicating an exothermic chemical reaction. The Euler and Martius procedure

specified potassium cyanide as the activator. Apparently, however, glucoreductone results even in the absence of cyanide; with alkali as the activator, some form of a Cannizzaro reaction evidently occurs.

Example 37. Exposed Kodak Azo E 25 seconds, and developed 5 minutes with Reductone Developer R-3 (20C). The silver image was warm toned and browner than Example 69. The paper stock was not tinted.

Example 38. Exposed Kodak Athena B 30 seconds, and developed 6 minutes with Reductone Developer R-3 (20C). The print was warm toned, and browner than Example 37. The paper stock was tinted.

REDUCTONE DEVELOPER R-4 FOR PAPERS

Reductone Developer R-2	1 liter
Sodium acetate, desiccated	65 grams

Acetic acid (28%); add until the solution turns blue litmus paper pink.
Sodium carbonate, monohydrate; add until the solution turns pink litmus paper blue. The pH of the developer will then be about 8.2.

To use, immerse the exposed paper in the Reductone Developer R-4 for about 15 minutes, the time and temperature being relatively unimportant. A suitable container for the developer is an ordinary beaker, and a 4 × 5 paper will require a full 600 ml beaker. The paper then will not float. No image will appear during this time. After 15 minutes, remove the paper, drain, and let dry face up. The image should begin to appear within one half to one hour, depending on the pH and the degree of exhaustion of the developer. If the image does not begin to reveal itself, add a gram of sodium carbonate; if it appears too soon, add a drop or so of acetic acid (28%). Let the image develop in the air for an hour, or until completely developed. If the paper becomes comparatively dry, and development is incomplete, soak the paper in the developer a second time for a few minutes, and again let it dry. When development is complete, place the print in the thiosulfate solution, avoiding the stop bath.

The developer, with use, tends to become more acidic due to the acidic nature of the oxidation products. This tendency is opposed by the buffer, sodium acetate, and it may be corrected readily by adding small quantities of sodium carbonate from time to time as needed.

Example 73. Exposed Kodak Azo E 15 seconds, and immersed the paper in Reductone Developer R-4 15 minutes (about 27C). On drying, the first indication of an image appeared in 38 minutes. After an additional drying period of 33 minutes, the print was soaked again in the developer for a few minutes, and dried further for one hour and 45 minutes. The image was not merely warm toned; it was entirely brown, or possibly reddish brown in color, with no trace whatever of black, the deep shadows being a very dark brown. The paper stock was not tinted, and there was little or no fog.

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THE USE OF PROTEOLYTIC ENZYMES FOR THE REMOVAL OF GELATIN FROM FILM BASE

Eugene Gansel*

ABSTRACT

In the reclamation of used film base, the process of separating the emulsion and noncurling gelatin layers from the plastic support must be controlled if the recovered material is to be re-usable. The most common methods of reclaiming film scrap have been evaluated. The use of proteolytic enzymes for the removal of gelatin layers from photographic films has been investigated. Economic use of these new "organic catalysts" and the need for satisfactory evaluation procedures and rigid process controls are discussed.

THE PURPOSE of the present study was to establish a reliable analytical method for the evaluation of commercially available proteolytic enzymes used in the removal of gelatin coatings as well as gelatin silver halide layers from photographic materials. It is only difficultly possible to remove such layers with straightforward chemical means (hot detergents, oxidizing agents, dilute acids, alkalies, salts, etc.). These procedures leave much to be desired.

In the main, film base consisting of cellulose esters is apt to be rather badly deteriorated by those drastic chemical treatments. As the result of the customary chemical treatments for the removal of gelatin, essentially two defects are inflicted on the film base (a) oxidative degradation, (b) hydrolytic decomposition of the cellulose esters. In both instances the reutilization of the reclaimed cellulose ester is jeopardized. The favorable solvent solubility of the original cellulose ester is generally impaired by the formation of carboxyl groups and hydroxyl groups respectively. In the latter case partial de-esterification takes place leading to a type of regenerated cellulose which is highly undesirable in the solvent soluble cellulose acetate dope. Such improperly reclaimed film base evidences itself in slugs, swollen particles, fibers, in a heterogeneous and often badly discolored dope. Experts in cellulose ester technology know how difficult and costly it is to purify such initially poor film dopes. It is therefore important that chemical degradation of the cellulose ester base is held to a minimum.

By the use of enzymes much more favorable, i.e. milder, recovery treatments at moderate temperatures may be afforded. Inadvertently, an improved film base material is recovered from photographic scrap. The use of enzymes has brought about efficient recovery procedures which make oxidation or over-treatment virtually impossible as these conditions would decompose the enzyme itself and thereby nullify its action.

It seems appropriate to give a brief definition of enzymes in general and of proteolytic enzymes in particular. Enzymes are water soluble, colloidal, organic catalysts produced by the living organism. Proteolytic enzymes are those that act on proteins or are specific for protein hydrolysis. It would go beyond the intent of this discussion to dwell upon the hundred year history of enzymes. Suffice it to mention that Pasteur still preached in 1870 that enzyme action was dependent on living cells, until Buechner in 1897 completely disproved Pasteur's vitalistic concept by showing that enzymes can be made to act in fermentation reactions without the presence of cell structures. Today enzymes are grown in chemical plants, just like penicillin molds, isolated and crystallized. Presently, many hundred of enzymes are known; however, only a relatively small number has found its way into industrial processes.[2,4,6,8]

Enzyme Action

One of the more important processes to which enzymes have been put to work was the desizing of cottons and synthetic yarns. This was done with amylolytic enzymes, those that specifically work on the digestion and hydrolysis of starches and starch gums into easily soluble sugars. The proteolytic enzymes came later into prominence. The degumming or defibrination of the natural silk fiber, long a process done by soaping and harsh alkali treatments, was ultimately replaced by the superior enzymatic degumming. Many more examples could be cited but the following should serve as illustrations:

Starch	$\xrightarrow{\text{Diastase}}$	Hydrolysis to maltose
Sugar	$\xrightarrow{\text{Invertase}}$	Hydrolysis to dextrose and levulose
Fat	$\xrightarrow{\text{Lipase}}$	Hydrolysis to fatty acids and glycerol
Urea	$\xrightarrow{\text{Urease}}$	Hydrolysis to ammonia and CO_2
Protein	$\xrightarrow{\text{Protease}}$	Hydrolysis to amino acids
H_2O_2	$\xrightarrow{\text{Catalase}}$	H_2O and oxygen
Luciferin (Firefly)	$\xrightarrow{\text{Luciferase}}$	Bioluminescence
Intestinal Worms	$\xrightarrow{\text{Ficin}}$	Protein hydrolyzates.

While the first five examples are drawn from industrial processes, the last three belong to the field of biochemistry.[8,9,10]

* Ansco Research Laboratories, Binghamton, New York. Presented at the PSA National Convention in New York, N. Y. 15 August 1952. Received 7 August 1952.

Enzymes are most remarkable substances. To understand their action one must know something of their properties. They are mostly colloidal in nature and are proteins themselves. Thus far they have evaded the organic chemist. No enzyme has been synthesized as yet. They are dependent on suitable substrates which in former times have been confused with nutrients. Because of this specificity an amyolytic enzyme would be quite ineffective on a protein substrate and vice versa a proteolytic enzyme would not be usable for the hydrolysis of starch. However, the picture is quite complex as it is frequently with nature's products. Many commercially produced enzymes are mixtures of individual enzymes which react on several substrates.

Esterification by Proteolytic Enzymes

An enzyme, as a true catalyst, is capable of hydrolysing a suitable substrate into smaller molecular aggregates. Also the reverse is possible. An enzyme is capable of synthesizing a larger molecule from simpler components. In nature, e.g. in the animal organism, such syntheses are carried on regularly. And in the laboratory the formation of ethyl butyrate from ethanol and butyric acid in the presence of lipase, a proteolytic enzyme obtained from the pancreas gland, has been accomplished.[1]

In the present work the confirmatory observation was made: A fruity and pleasant smelling ester was produced when enzyme-gelatin digests were allowed to stand in contact with ethanol at room temperature for several hours. The indication was that we obtained the synthesis of ethyl citrate by proteolytic enzyme catalysis on the liberated citric acid from the citrate buffer and the ethanol present in the mixture whose pH had been allowed to drop on the acid side.

Influence of Substrate

Being concerned with the evaluation of several commercially available proteolytic enzymes, it was logical to think of casein as a suitable substrate. It is a protein obtainable in rather pure form from milk. Also a number of enzyme evaluation studies have been based on casein hydrolysis. Northrup's casein solubilization procedure is probably the best known.[2,3,4]

The evaluation work started out with casein and compared the effect of enzymatic action with that on gelatin. Surprisingly the results were very divergent. Below are listed 6 proteolytic enzymes in their order of rank in regard to activity. They were tested under carefully controlled conditions.

Casein Hydrolysis		Gelatin Hydrolysis	
Enzyme A	90%	Enzyme A	99%
" B	80%	" D	98%
" C	75%	" E	90%
" D	73%	" C	80%
" E	62%	" B	70%
" F	45%	" F	50%

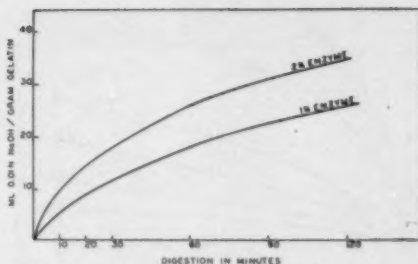The rank order tabulation shows how an erroneous conclusion would be drawn if a certain enzyme were to

Fig. 1. Reaction velocity of Rhozyme P-11 enzyme at 40C on 4.3% gelatin solution (pH 8). Determined by formol titration.

be tested by the casein hydrolysis method if it is intended to be used for gelatin removal from film base. We attribute the observed difference in behavior to the different chemical composition of the two proteins.[5]

	Casein	Gelatin	
Neutral Amino Acids	52.0%		73.0%
Glycine	0.5%	24.0%	
Alanine, Serine	8.5	11.0	
Valine, Leucine	22.0	6.0	
Proline, Oxyproline	11.0	32.0	
Tyrosin & others	10.0	0.0	
Basic Amino Acids			
Histidine, Arginine, Lysine	15.0%		18.0%
Dicarboxylic Amino Acids			
Aspartic & Glutamic Acids	33.0%		9.0%
	100.0%		100.0%

Therefore efforts were concentrated on working out a procedure for testing enzymes in their action on gelatin exclusively.

Reaction Velocities

An enzyme, being a catalyst, speeds up the hydrolysis of gelatin tremendously. It was found that the measurement of the initial hydrolysis is more important than to follow the reaction through to an end point or to a maximum which is asymptotically reached. Figure 1 illustrates the point.

In the first 5 minutes of digestion time hydrolysis of the gelatin is more than doubled. At 10 minutes digestion time proportionate conditions prevail, whereas at longer digestion periods proportionality no longer holds. The curves flatten out to reach maximum values after 3 hrs. digestion time. From these curves it is seen that enzymatic activity rates decrease with time. Only in those cases where enzymes of very low activity were tested did the activity-time relationship approach a linear function.
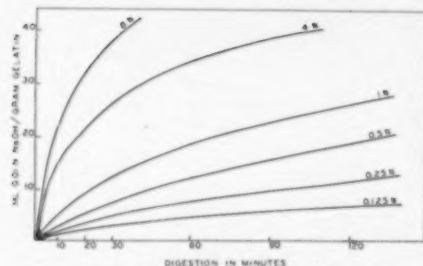
Fig. 2. Effect of enzyme concentration on velocity of gelatin hydrolysis. Data are for Rhozyme P-11 at 40C using 4.3% gelatin solution (pH 8), determined by formol titration.

Enzyme Concentration

With large enzyme concentrations the rate of reaction proved to be almost uncontrollably rapid in the initial stages of the digestion. However, doubling the enzyme concentration does not necessarily double the reaction rate. Figure two shows that in order to attain the same level of hydrolysis (e.g. 40 ml 0.01 N NaOH per g gelatin) enzyme concentrations of 8%, 2%, 1%, 0.5% will require 5 min., 10 min., 75 min., and 135 min. digestion time. This means that the corresponding reciprocal digestion times or reaction velocities will range in the order of 200; 100; 13; 7; for the above concentrations. With other words: To double the reaction rate, the enzyme concentration must be quadrupled.

Substrate Concentration

As most test methods are based on 4 to 5% gelatin concentrations, standard 4.3% gelatin solution was adopted for our tests.

In the literature[6] it has been reported that both low and high substrate concentrations will impair enzyme activity. A somewhat analogous observation was made in one of our experimental series. See Figure 3. Three different gelatin concentrations (0.43%, 1.16%, 4.3%) were subjected to the same enzyme concentration (8% based on gelatin content) at the standard digestion conditions at pH 8 and 40C.

At equal acidity levels (e.g. 100 ml 0.01 N NaOH per g gelatin) the three gelatin substrate concentrations show these relative reaction velocities:

	Reciprocal of Digestion Time $\times$ 1000
0.43% Gelatin	5
1.16% "	30
4.30% "	13

The medium gelatin concentration showed highest enzymatic activity in the experiment.

Influence of pH

Proteolytic enzymes are said to be most active over a wide pH range. Experiments (see Figure four) showed

the very decided preference for pH 8. The curves for the 2% enzyme concentrations illustrate that the same acidity or hydrolysis level of substrate is reached in 12 minutes at pH 8, whereas it takes 55 minutes at pH 5. Similar results were obtained with 1% enzyme concentrations. If expressed in relative reaction velocities (Reciprocal of Digestion Time $\times$ 1000) the following figures ensue:

	Relative Reaction Velocity	
	2% Enzyme	1% Enzyme
At pH 8	90	30
At pH 5	20	8

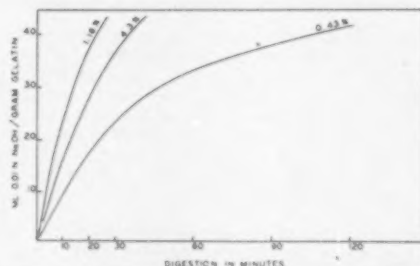The data indicate that the reaction velocity is more than 4 times greater at pH 8 than at pH 5.

Fig. 3. Effect of gelatin substrate concentration (pH 8) on the velocity of hydrolysis using 8% Rhozyme P-11 at 40C (based on gelatin content). Determined by formol titration.

Influence of Temperature

Reaction rates of enzymatic digestions are materially influenced by temperature. A 10C rise for example, from 40 to 50C, may increase the rate of reaction from 1.5 to 2 times.

Experiments were carried out at 40C, allowing a plus minus deviation of 1C. Realizing that this much temperature variation may influence the activity results as much as 15%, careful temperature control was exercised in the evaluation runs. No attempt was made, however, to determine the temperature optima for all the enzymes which were investigated. To limit the work, 40C was arbitrarily selected with the understanding that the testing was on a rather broad temperature plateau of activity which would be unencumbered by inactivation effects frequently encountered at or near the optimum temperature.

Influence of Hardening Agents

In photographic emulsions various hardening agents are used in order to render the sensitized layers less injurious to mechanical abrasion. These hardeners which are mainly aldehydes render gelatin less soluble or even insoluble. If this hardening action proceeds too far, a leather-like gelatin resin is produced which requires drastic treatments to remove in the film scrap recovery process. How gelatin behaves under the influence of an aldehyde hardener is illustrated in Figure five.

Equal Money Value Comparisons

For practical reasons the 6 different enzymes investigated were brought on one and the same economic denominator; they were tested in concentrations of equal money value equivalents:

    32.00% Serizyme Regular
    20.00% Rhozyme PF
    11.00% Serizyme Concentrated
     2.16% Takamine #1
     2.16% Takamine #2
     2.00% Rhozyme P-11

These concentrations were reacted on 4.3% gelatin substrate at pH 8 at 40C. The degree of gelatin hydrolysis was measured as acidity increase by means of the formol titration procedure which will be explained later.

The results, plotted in Figure six, illustrate the high reaction rates in the early period of the digestion runs. Here the activity differences of the various enzymes show up most decidedly. The data also emphasizes the need to rely on the results of short digestion runs rather than on periods in excess of 1 hour.
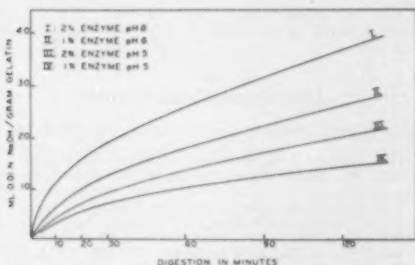
Fig. 4. Influence of pH on velocity of gelatin hydrolysis by Rhozyme P-11 in 1% and 2% concentrations at 40C. Determined by formol titration.

Formol Titration

A modification of the original Soerensen formol titration was worked up in the present study.[6,7] The method is based on measuring the apparent free acidity formed in the hydrolysis of proteins. This is accomplished by arresting further hydrolysis with formaldehyde addition and titrating the acidity with standard alkali. A blank digest is run under the same conditions. The difference of sample from blank acidity is the increased acidity and expressed in terms of ml 0.01 N NaOH per g gelatin. For the theoretical background of the method the original literature must be consulted as it would be outside the scope of the present discussion.[4,5,6,7,8]

The following is a condensed version of the modified formol titration procedure used in these experiments.

Apparatus

A double necked 500 ml flask is clamped to a constant temperature water bath adjusted to 40C. Through one
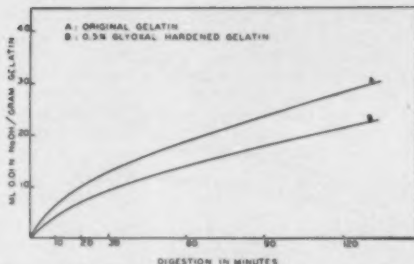
Fig. 5. Influence of gelatin hardening treatment on the velocity of hydrolysis by Rhozyme P-11.

neck of the flask, an electrically driven glass propeller is inserted. Through the other neck a thermometer extends to the bottom of the flask for measuring the temperature of the digestion mixture. By way of the same neck all charging and withdrawing of solutions is done. The digestion mixture is made up outside the digestion flask. A cut-off recalibrated 50 ml pipette is held in readiness for withdrawing aliquots from the digest at regular time intervals.

Solutions

Buffer Solution (pH 8)
    22 g Citric acid monohydrate
    13 g Caustic soda pellets
    28 g Na$_2$HPO$_4$.12H$_2$O
     5 g Boric acid
    made up to 1 liter with distilled water and pH adjusted prior to making up to final volume.
Formaldehyde-Phenophthalein Solution
    450 ml 40% Formaldehyde (Du Pont)
     72 ml 1% Phenolphthalein in ethanol
0.5 N NaOH Solution
1% Enzyme Stock Solution
    5 g of the enzyme to be tested are weighed to the nearest 0.01g and transferred to a porcelain mortar. With small amounts of water a paste is ground and transferred with repeated portions of water to a 500 ml volumetric flask. The stock solution is kept refrigerated. Before pipetting an aliquot portion, the contents of the flask are well shaken but not filtered.

Procedure

As substrate a 4.3% (photographic grade) gelatin solution is made up by soaking 15 g in 150 ml distilled water of room temperature for 30 minutes in a 500 ml Erlenmeyer flask. The swollen mass is melted on a steam bath by swirling the flask. The solution is cooled to 45C and transferred into the double necked flask. For rinsing the Erlenmeyer, 150 ml water of 40C is used in several portions. 60 ml pH 8 Buffer Solution are added. Agitation is started and the temperature is adjusted to 40C. The digestion volume is now so adjusted that the volume will be 320 ml. Lastly, a 30 ml aliquot of the 1% enzyme stock solution is pipetted into the digestion flask. This instant is noted as the digestion start. The final digestion volume should now be 350 ml.
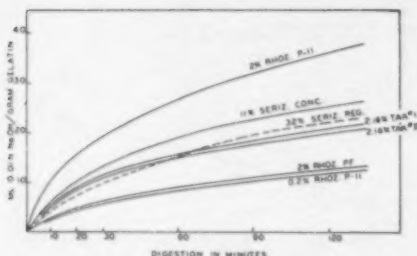
Fig. 6. Hydrolysis rates of different enzymes in concentrations representing equal material cost.

In intervals of 5, 10, 20, 30 and 60 minutes 50 ml withdrawals are made with the cut-off pipette using a vacuum line for quick aspiration. The digest withdrawals are run at once into 250 ml Erlenmeyers, each containing 22 ml of the Formaldehyde-Phenolphthalein solution. The action of formaldehyde stops all digestive action at the instant of pipetting the digest aliquot into the Erlenmeyer flask.

Titration

The titrations of the 5 Erlenmeyer flasks are conveniently made at the end of the digestion run. Each 50 ml aliquot representing $^1/_7$ of the original 15g gelatin present should titrate from 3 to 7 ml 0.5 N NaOH depending upon the degree of hydrolysis.

Blank

In the same described manner a blank run is made in the double necked digestion flask. But instead of adding the 30 ml enzyme aliquot, 30 ml water are used.

Calculation

The titration value of the blank is subtracted from the titration value of the sample. This difference is converted into ml 0.01 N NaOH per g gelatin and plotted on graph paper using 2-inch spacings for each 10 ml 0.01 N NaOH on the ordinate and 1-inch spacings for each 10 minute time interval on the abscissa. In such a large scale graph, the values, particularly those at the lower

part of the curve, can be satisfactorily read for determining the slope of the curve.

A proteolytic enzyme giving a formol titration value of more than 5 ml 0.01 N NaOH per g gelatin in 5 minutes digestion time is considered an effective enzyme. It shows the following titration and hydrolysis values:

Digestion Time	0.01 N NaOH per g gelatin	Hydrolysis
5 min.	5.5 ml	52.0%
10 "	10.5 "	61.5%
20 "	17.5 "	73.0%
30 "	23.5 "	82.5%
60 "	35.7 "	97.0%

The hydrolysis values were obtained by Bogue's ethanol precipitation method.[6]

Summary

A procedure is presented for the quantitative evaluation of the activity of commercial proteolytic enzymes. The procedure is based on the formol titration method and is characterized by its relative simplicity. The procedure was tested on enzymes obtained from Rohm & Haas, Takamine Labs. and Wallerstein. The procedure is capable of measuring the activity retarding effect of hardened gelatin as it would be encountered in photographic films.

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COLD STORAGE OF PHOTOGRAPHIC FILM

J. M. Calhoun*

IN RECENT YEARS there has been an increase in the use of refrigerated storage for unexposed photographic film supplies to avoid or reduce undesirable changes which can occur due to prolonged storage at elevated temperatures. Questions frequently asked are: Must the temperature be kept above 32 F? Does moisture condensa-

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tion occur inside the package? Can the film be harmed in any way by refrigeration? It is the purpose of this article to attempt to answer these questions, explain the principles involved, and to dispel some commonly held fallacies concerning the cold storage of film.

It is well known that photographic films, regardless of the manufacturer, are perishable. Changes in speed and contrast (usually a decrease) and a gradual growth of

fog occur with age. This is particularly serious with multilayer color films because the characteristics of one layer may change at a different rate than those of another layer and so upset the color balance of the film.

Adverse storage conditions can cause much greater changes in film properties in a relatively short time than would ordinarily occur during the entire dated life of the film when stored at ordinary room temperatures, for example, not above 75 F. A lowering of the storage temperature definitely retards these changes and, therefore, preserves the characteristics of the film in a more nearly fresh condition. It is for these reasons that the film manufacturer recommends proper storage conditions for his product, and prints an "expiration" date on the package so that the film can be used before it has become too old.

Expiration Dating

The "expiration date" assigned to films by the Eastman Kodak Company, for example, is determined by storage tests made at a variety of temperatures and relative humidities. The dating is ascertained on the basis of the time a given product will withstand average or typical trade storage conditions in the United States, and still yield a satisfactory result. It does not mean that expired film which has been stored at these conditions will produce results identical with fresh film. The time to expiration varies depending on the properties and requirements of the particular product.

Protection from Moisture

Moisture and heat are the two factors in film storage which contribute most to deterioration. The moisture content of film as it leaves the factory is very precisely controlled at just the right level to insure the best possible performance. This moisture level, which corresponds to equilibrium with air at a relative humidity varying from 40% to 60% for different types of film, should remain constant during storage. Higher relative humidities accelerate deterioration and cause various physical defects. Lower relative humidities increase the susceptibility of film to static markings, curl, brittleness and so forth. Fortunately, film can be protected from moisture damage by the manufacturer through the use of vapor barrier packaging.

Moisture vapor protection for film has been improved greatly in recent years so that now most films after first being conditioned at the desired humidity are packaged in sealed metal cans or tubes, sealed foil bags, or other suitable vapor barriers. Until such packages are opened, moisture from humid air or damp storage locations, even in tropical climates, cannot penetrate and harm the film. Of course, all films are not completley protected from moisture by perfect vapor barriers and the photographer should know, either by the construction of the package or by the recommendations of the manufacturer, whether his film is completely protected from moisture vapor or not.

Protection from Heat

The protection of film from heat during storage is something over which the film manufacturer has no control and, therefore, is a problem for the photographer. The higher the storage temperature the more rapidly films deteriorate. Even though most films will yield satisfactory results if stored at average room conditions until their expiration date, considerable improvement is obtained if lower storage temperatures are used. The Eastman Kodak Company recommends that most films be stored according to the following schedule:

For storage periods up to:	2 months	6 months	12 months
Keep films below:	75 F	60 F	50 F

For certain special films such as some high speed black-and-white films, some color films[1], etc., or in cases where longer storage periods are desired, still lower temperatures are recommended, for example, a temperature of 0 F. In this way maximum quality in even the more critical products can be maintained for longer periods of time, often well beyond the expiration dating of the film.

Refrigeration

Film can be stored safely in any suitable refrigerator, *provided that the film is sealed in a vapor-tight package or container.* Refrigerators are frequently humid, particularly household refrigerators containing foods and liquids, and film stored in unsealed or porous packages will absorb moisture from the air and damage may result. Film which is not factory sealed in vapor-tight packages should be placed in a can or jar which can be closed with an air-tight lid before it is put in the refrigerator.

Household refrigerators usually operate at about 40 F to 50 F and are quite satisfactory for the storage of most films, with the proviso mentioned in the preceding paragraph. For specially sensitive films, or films to be stored for extensive periods, a deep freeze unit of the type available for frozen foods operating at 0 F to −10 F. is recommended.

Does Water in Film Crystallize Below 32 F?

The answer to this question is "no," at least insofar as film at its normal moisture content is concerned. The question is asked frequently because people know that water in food does crystallize and unless food is quickly frozen the ice crystals may be large enough to rupture the cell walls which promotes spoilage. At first glance it might seem that a similar process could occur with film and the sensitive emulsion be damaged.

While the water content of fruit and vegetables is of the order of 90%, the water content of a typical photographic emulsion in equilibrium with air is much less[2] as indicated below:

Relative Humidity of Air	Equilibrium Moisture Content of a Photographic Emulsion
20%	5%
50%	8%
80%	15%

This is undoubtedly the reason that ice crystals or damage from ice formation has never been found in photographic film stored at below freezing temperatures. The small amount of moisture normally found in photographic emulsions or in dry gelatin is not present in the form of liquid droplets but is molecularly adsorbed

within the colloid. Furthermore, studies made by Moran[3] have shown that gelatin solutions containing less than 34% water cannot freeze at any temperature down to that of liquid air.

Laboratory experiments have been designed to verify the safety of storing sensitive films at low temperatures. In one experiment made by the Eastman Kodak Company in 1939 several types of film were stored for three weeks completely surrounded with dry ice (solid carbon dioxide) in an insulated container. Thermocouples indicated the film to be at a temperature below −100 F. After removal the film was subjected to microscopic examination and no change in the emulsion structure found. Exhaustive photographic tests, and physical tests made on the film before and after processing, showed no detrimental effect of any kind. Since that time there has been considerable practical experience in the storage of film at low temperatures, in some cases for as long as three years at −10 F. Never has any detrimental effect been found, *provided that the film was protected from the penetration of moisture vapor from outside the package.* It makes no difference whether the film is cooled slowly or is quickly frozen in dry ice, or how low a temperature is used.

Dry ice has been used by the Eastman Kodak Company to ship various color films to different parts of the United States in hot weather without loss of quality. Dry ice has also been used satisfactorily to protect color motion picture film from heat during air shipment from a production location in Australia to Hollywood for processing.[4]

Condensation When the Package Is Opened

Moisture must not be allowed to condense on sensitive photographic film or injury may result. It is well known that moisture from the air condenses in droplets on a cool surface, such as the outside of a glass of cold water. Moisture condenses on a surface when the temperature of the surface is below the dew point of the surrounding air. The dew point of air is determined by its moisture content and may be as low as 10 F inside a heated building in winter, but in summer it may be as high as 75 F in temperate climates and 90 F in tropical climates. Moisture from the air will condense on an object removed from a refrigerator operating at a temperature below the outside dew point.

Moisture condensation on film removed from a refrigerator may be prevented easily by allowing the package to warm up to room temperature before it is opened. The warm-up time depends on the thickness of the package, how well it is insulated, the temperature difference, etc. For film in commercial packages the approximate warm-up time is as follows:

	Warm-Up Time	
	For a 25 F Rise	For a 100 F Rise
Single rolls of 616, 620, etc.	20 minutes	30 minutes
Single 16mm roll	1 hour	1½ hours
Single 25-sheet box of film	1½ hours	2 hours
Single 100-sheet box of film	3 hours	5 hours
Single bulk 35mm × 100 ft. roll	4 hours	6 hours

Although moisture condensation on glass, metals and other relatively non-porous materials is readily visible as tiny droplets of water, it is generally not visible on porous materials such as unglazed paper, corrugated cartons, cardboard boxes, etc. This is because in the latter case the moisture is absorbed rapidly by the material and droplets of water do not have time to form. Tests were made with film samples cooled to 0 F then opened quickly in air at 70 F and 70% relative humidity (dew point, 60 F). It was found that moisture droplets were quite visible on film base, only very slightly visible on a gelatin backing on film, and frequently quite invisible on the emulsion surface where rapid absorption occurs. This fact tends to lessen the chance of water spotting gelatin-backed films as a result of moisture condensation, but an increase in moisture content of the film is undesirable even if water droplets do not form.

Condensation Inside the Package

When air is cooled, the relative humidity rises and at the dew point or below moisture condenses on any convenient surface. Because of this fact people have sometimes reasoned that when a package of film is placed in a refrigerator the moisture in the air *inside* the package will condense on the film and damage it. Film is usually packed in rooms conditioned at about 70 F and 45% to 60% relative humidity. The dew point for these conditions is 48 F to 56 F and if the air is cooled below these temperatures it must give up some of its moisture. Hence, it is argued that film should not be refrigerated.

There is a simple fallacy in this argument. Actually there is so little air present inside the film package, and the quantity of moisture present in this air is so infinitesimal that its effect is negligible. This can be demonstrated readily by a few examples

Example 1.—A box of 4″ × 5″ Sheet Film

Ten sheets of film interleaved with paper are packed between two stiffener boards (cardboard) inside a heat sealed aluminum foil envelope.

Volume of envelope as packed	=	110 cc
Volume of film, paper, and cardboard	=	80 cc
Volume of air inside envelope	=	30 cc

The moisture content of air at 70 F and 50% relative humidity = 4.0 grains per cu. ft.[6]
For 30 cc of air this equals:

$$\frac{4 \times 30}{28,320} = 0.00424 \text{ grains} = 0.000275 \text{ grams of water.}$$

Let us assume that all of this water is condensed out when the package is cooled. The pieces of cardboard on either side of the film weigh 5.6 grams each or 11.2 grams. Moisture equilibrium curves for this material show that it has a water content of 7.75% at 50% relative humidity and 7.9% at 51% relative humidity. Hence,

Amount of water in cardboard at 51% R.H. = 0.885 grams
Amount of water in cardboard at 50% R.H. = 0.868 grams
Difference for 1% R.H. = 0.017 grams

Since 0.017 grams of water increase the equilibrium relative humidity of the cardboard 1%, 0.000275 grams of water increase the equilibrium relative humidity of the cardboard only by 0.016%.

Even if the film were not protected by the cardboard but only by a single sheet of interleaving paper on each side the result would be similar. The two sheets of

paper weigh 1.762 grams. The moisture content of interleaving paper is 6.75% at 50% relative humidity and 6.9% at 51% relative humidity. Hence,

Amount of water in paper at 51% R.H. = 0.122 grams
Amount of water in paper at 50% R.H. = 0.119 grams
Difference for $\overline{1\%}$ R.H. = 0.003 grams

Since 0.003 grams of water increase the equilibrium relative humidity of the paper 1%, 0.000275 grams of water increases the equilibrium relative humidity of the paper only 0.1%.

Example 2.—A 20-exposure roll of 135 film.

This type of film is wound in a magazine and usually packed in a tight aluminum can. A tab of film extends out of the magazine for threading and there is no paper wrapping present. This package represents a relatively high ratio of free air space to film.

Volume of can = 33 cc
Volume of magazine = 8 cc
Volume of free air space = $\overline{25}$ cc
Weight of film tab outside magazine = 0.466 grams

Using the same calculations as in Example 1, we find the water content of the air inside the can at 70 F and 50% relative humidity to be 0.00023 grams.

Let us assume that all of this water condenses on the film tab when the container is cooled and none on the walls of the can. From moisture equilibrium curves we find the films contains 2.8% water at 50% relative humidity and 2.9% at 51% relative humidity. Hence,

Amount of water in film tab at 51% R.H. = 0.0135 grams
Amount of water in film tab at 50% R.H. = 0.0130 grams
Difference for $\overline{1\%}$ R.H. = 0.0005 grams

Since 0.0005 grams of water increase the equilibrium relative humidity of the film tab 1%, the 0.00023 grams of water in the free air space in the can would increase the equilibrium relative humidity of the film only a half of one percent—truly a negligible amount. Furthermore, the tab itself is not used for picture taking.

It cannot be argued that film or paper absorbs less moisture at constant relative humidity at low temperatures since the small effect of temperature on this relationship is in the opposite direction.

The fear of moisture in the air inside a film package condensing on the film when cooled in a refrigerator and causing damage is entirely fallacious from a theoretical standpoint. There is simply not enough water in the small amount of air available. This has been confirmed by adequate laboratory test and practic l experience. If a square inch of film were packed in a barrel of air the situation would be different.

It is possible that the false notion that moisture in the air inside the film package would damage the film and, therefore, film should not be refrigerated, arose from a different cause. As pointed out earlier, if the film is not protected by a moisture-vapor-proof package, additional moisture can penetrate to the film from outside the package while stored in a humid refrigerator. This is an entirely different problem which can be solved by proper packaging.

Storage after Refrigeration

The question is often asked whether film stored for some time in a refrigerator and then removed will keep any better or worse than film which has never been refrigerated. The answer to this depends primarily on whether the film is protected by its package from possible moisture penetration during the cold storage period. If such protection did not exist the film might absorb enough moisture during refrigeration that, even if deterioration had not occurred by the time the package was removed, it would be accelerated at normal or summer temperatures after removal. In such cases the film might be found eventually in poorer condition than if never refrigerated.

On the other hand, tests indicate that films which are stored in a refrigerator in moisture-vapor-tight packages and then removed will change in speed and contrast thereafter along the same rate curves which were interrupted during the cold storage. In this respect the period of refrigeration neither improves nor harms subsequent keeping at normal temperatures. However, some types of films have been observed to develop slightly more fog when kept at elevated temperatures after long periods of refrigeration than could be accounted for by the higher storage temperature alone. Cold storage thus does not completely arrest all changes which may occur in a photographic emulsion. For this reason it is recommended that film which is near its expiration dating be used soon after it is removed from cold storage.

In conclusion it may be said that cold storage is a safe and satisfactory means of prolonging the useful life and safeguarding the quality of sensitized photographic material provided that the precautions mentioned are taken. The photographer need have no fear that the film will be harmed by using the storage temperatures recommended by the manufacturer for the particular product.

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Properties of Developing Agents.   II.   Paraminophenols[*]

R. W. Henn

SUMMARY

The nine paraminophenols examined fall into two classes according to the nature of the substituent groups, which may be (a) non-ionic, or (b) ionic, in character. The agents of Group (a) initiated development rapidly with little induction period, their activity increased smoothly over a wide pH range, and the density:log-time curves characteristically had slope values of 1.3 or 2.6.

The substituents of Group (b) included sulfonic and carboxylic acid groups. These agents showed appreciable induction periods, were more dependent on pH changes, and the most characteristic slopes of the density:log-time curves were 2.6 and 3.3. These differences are explained on the basis of the ionic charge theory of development, Group (a) developing (1) without charge, or (2) with a monovalent charge, while Group (b) develops with (1) a monovalent, or (2) a divalent charge.

Oxidation proceeded very differently from development, most of the agents oxidizing at a similar rate in spite of wide differences in developing activity. Loss of activity was accompanied by parallel discoloration. Two of the agents did not oxidize any more rapidly at a pH of 12.8 than at 11.5, although their developing activity increased.

T HE FIRST paper in this series[1] described the photographic properties of a number of hydroquinones. Most of these were found to develop when the pH was increased to about 9, and were then strongly affected by pH changes up to about 11.5, but were almost unaffected by further elevation of pH. Development characteristically proceeded rapidly, but only after a considerable induction period, and was a linear function of the logarithm of the developing time. The slopes of these density:log-time curves were but little affected by changes in pH, or even by the nature of the developing agent, the wide range of activity obtained being primarily due to changes in the induction period. The rates of oxidation were measured and the solutions were found to lose activity more rapidly than they discolored.

The present paper considers the photographic properties of nine paraminophenols. A third in the series will consider combinations of the paraminophenols with the hydroquinones.

The paraminophenols employed are sketched in Table I. They include paraminophenol itself (I), and compounds in which the amino group has been variously substituted: by methyl (II; this is the popular developing agent, Elon[†] or Metol), by β-hydroxyethyl (III), by β-aminoethyl (IV), by sulfomethyl (V) (more precisely named "sodium p-hydroxyphenylaminomethane sulfonate"), by acetic acid to form the glycine (VI), and by both methyl and acetic acid groups (VII). Compound VIII represents II modified by the substitution of a chlorine atom for a hydrogen in the benzene nucleus, while compound IX contains a nuclear sulfonic acid group. Compounds I, II, and VI represent commercial samples, while the others were synthesized by the Chemical Plant of the Eastman Kodak Company.

The methods of investigation and evaluation were considered in the first paper of this series. They include the use of a simple, positive emulsion, and the employment of density for a fixed exposure as the criterion of the degree of development. The selected exposure is circled

in the characteristic curves of Figure 1, where it is seen to lie high on the straight-line portion. Aeration tests were carried out by exposure in unstoppered flasks, while the solubility measurements were made in a special high-salt developer.

The basic developer solution, in which the sensitometric measurements were made, contained 0.02 mole of
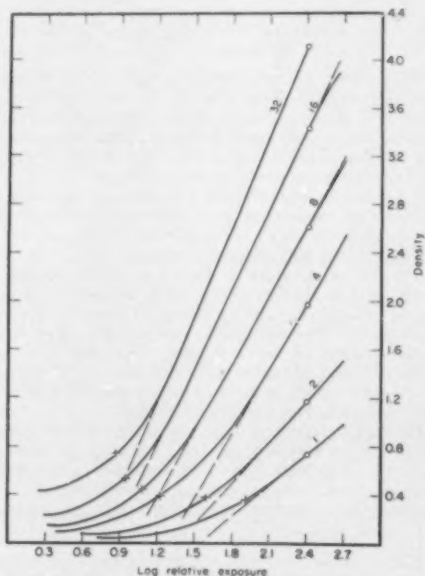

Fig. 1. Typical Group of H. & D. Curves (Elon, pH = 10.0). The fourth exposure step is circled. It is the density of this step which has been used as the measure of development throughout this paper. The speed point, determined as customary for this material, at a density of 0.3 above fog and base is marked with a cross.

Table I

THE DEVELOPING AGENTS

No.	Formula	Mol. Wt.	Name	pK
I.	HO⟨ ⟩NH$_2$.HCl	145	p-Aminophenol	
II.	HO⟨ ⟩NHCH$_3$.^{1}/$_2$H$_2$SO$_4$	172	p-βMethylaminophenol (Elon, Metol)	10.25
III.	HO⟨ ⟩NHCH$_2$CH$_2$OH.^{1}/$_2$H$_2$SO$_4$	202	p-Hydroxyethylaminophenol	10.3
IV.	HO⟨ ⟩NHCH$_2$CH$_2$NH$_2$.^{1}/$_2$H$_2$SO$_4$	201	p-β-Aminoethylaminophenol	...
V.	HO⟨ ⟩NHCH$_2$SO$_3$Na	225	p-Sulfomethylaminophenol, sodium salt	10.3
VI.	HO⟨ ⟩NHCH$_2$COOH	167	p-Hydroxyphenylglycine (Glycin)	...
VII.	HO⟨ ⟩N(CH$_3$)CH$_2$COOH	181	N-Methyl-p-hydroxyphenylglycine	...
VIII.	HO⟨ ⟩NHCH$_3$.^{1}/$_2$H$_2$SO$_4$ Cl	207	4-Amino, 2 (or 3) chlorophenol	8.8
IX.	HO⟨ ⟩NHCH$_3$ SO$_3$H	203	4-Aminophenol-2-(or 3)sulfonate	10.3

developing agent, 0.2 mole of sodium sulfite, 0.1 mole of an appropriate buffer, and sodium hydroxide as needed to neutralize the acid salts and phenolic hydrogen. The acidity of the phenol was considerable, the pK, or half-neutralization point being about 10.3 for all of the agents except the chloro-compound, VIII. Like chlorohydroquinone, this had a strongly acidic hydrogen and a pK value of about 8.8.

Experimental Results

1. Developing Activity

The density of the fourth step (see Figure 1) including fog is plotted against the logarithm of the developing time in Figure 2 for various pH levels. The following observations appear noteworthy:

(a) The induction period, before the image appears, is characteristically short (I, II, III, IV, VIII) except where a charged ion—carboxy or sulfonic—is present (V, VI, VII, IX). This latter group more closely resembles the hydroquinones in this respect. This is in agreement with James,[2] who has showed that glycine (VI) resembled hydroquinone in ionic charge and induction period.

(b) The density:log-time function (a measure of developing rate) is almost entirely linear, with the exception of a short toe portion. However, the slope of these lines is usually 2.6 or 1.35 density units per log-time unit, whereas with the hydroquinones it was 3.3 $D/\log t$. It will be noted that the lower value of slope applies to pH values of 8.5 or lower, the steeper slope to pH = 10.0 or higher, while with the most alkaline glycine developers (VI and VII, pH value of 12.8), the steep slope (3.3) of the hydroquinones is attained.

(c) The relative activity of the several agents and the influence of pH on activity are affected by the criterion selected for its measurement. The values of Table II and Figure 3 are based on the time required to reach a density of 2.0, which corresponds to the recommended development of this material (Kodak Fine Grain Positive Film). Agent (II), p-methylaminophenol, is seen to be the most active of the group. It has a readily measurable activity at a pH of 7, and becomes increasingly active as the pH is raised, throughout the entire range investigated.

Paraminophenol itself (I) and the hydroxyethyl-p-aminophenol (III) produce curves closely approximating those of the methyl compound (II) but displaced by 1.0 or 0.5 pH units, or in terms of developing times, they have one half or two thirds of its activity. Agent (IV), β-aminoethyl-p-aminophenol, shows certain peculiarities, which can be associated with the presence of the aliphatic amino group in its molecule. This accelerates development as the pH is raised but makes it much less selective (Fig. 4). The remaining compounds all contain charged ions and tend to be rather less responsive at high pH, particularly the glycines (VI and VII), which approach the hydroquinones in this respect. The activities of these several agents averaged (Table II) one fourth to one third that of No. II (Elon).

2. Selectivity

The fog produced by these agents at two degrees of development is plotted in Figure 4 as a function of the pH. All developing agents become less selective as the pH is increased, but this decrease in selectivity is not serious except for IV where, as suggested above, the

Table II

ACTIVITY

Agent	Min. for $D = 2.0$, at pH						Activity vs. Elon				Average
	7.0	8.5	10	11.5	12.8						
I.	..	55	9	3.1	1.9	...	0.22	0.47	0.67	0.74	0.53
II.	60	12	4.2	2.1	1.4	1.0	1.0	1.0	1.0	1.0	1.0
III.	140	18	4.8	2.8	1.8	0.43	0.68	0.88	0.75	0.83	0.71
IV.	130	40*	5.5	..	..	0.46	0.30	0.77	..	..	0.51
V.	..	32*	16	5.2	3.4	...	0.04*	0.26	0.41	0.41	0.36
VI.	..	70*	11	5	4	..	0.02*	0.38	0.42	0.34	0.38
VII.	60*	64	11	7.4	8	0.06*		0.38	0.28	0.18	0.26
VIII.	..	75	22	7.2	4		0.16	0.19	0.29	0.35	0.25
IX.	..	80	15	6	4		0.15	0.27	0.35	0.35	0.28
Hydro-quinone	..	....	14	4	4		0.005*	0.29	0.52	0.35	0.39

* For $D = 0.5$; omitted from average.

presence of the primary aliphatic amine becomes important as the developer becomes increasingly alkaline. The p-aminophenols have produced only about one half the fog values found for the hydroquinones and, in general, the lower the activity of the agent, the lower is the fog.
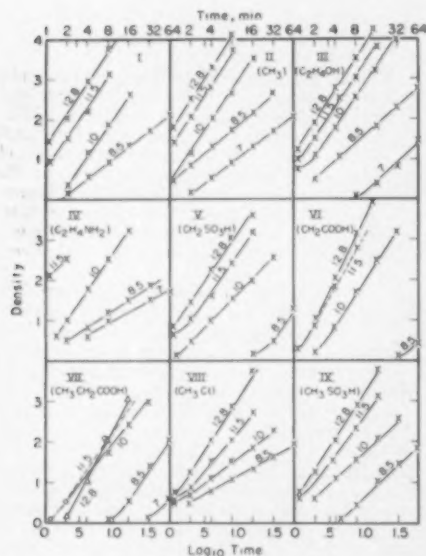

Fig. 2. Density: Log-Time Curves. The density of the fourth step has been plotted against an exponential progression of developing times. Note the "minute" scale at the top and the "log minute" scale at the bottom. The slope and displacement of these curves do much to establish the characteristics of the developer. The point at which the curves cross the density of 2.0 has been used as a measure of the "activity," while the slope of the line establishes the "rate" of development. The numbering of the agents is that of Table I, while the nature of the substituents is also indicated.
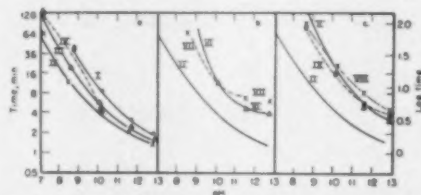

Fig. 3. Activity vs. pH. The time to reach a density of 2.0 has been plotted as a function of the pH. The numbering is as in Table I. Note that the time plot is, as in Fig. 1, again logarithmic.

3. Contrast and Emulsion Speed

As with the hydroquinones, the contrast produced was not primarily a function of the developing agent. The gamma obtained was usually about 2.0, with rather higher values being produced under restrained conditions, that is at low pH or with the addition of bromide. This value is also similar to that obtained for the hydroquinones. The emulsion speeds were also generally close at equal degrees of image density, some loss in speed being noted in the slowly acting pH = 7 developers, where the solvent action of the sulfite becomes important.[8]

4. Aeration Properties

The loss of developing activity of the p-aminophenol solutions was marked by a corresponding discoloration, the closeness of the two being dependent on the criteria of measurement selected. There was no marked exception to this but it was earlier found that the hydroquinones tended to lose activity completely while discoloring only slightly. Figure 5 directly compares hydroquinone with Elon (II). Note the rapid drop in activity or image density (D), of the hydroquinone as compared with the slow change in hue (H). On the other hand, in the case of Elon, the curves are close together.

The rate of oxidation of the various agents was found to increase with pH (Figure 6) but the change did not parallel the activity-pH curves. For example, Elon (II) and the hydroxyethyl compound (III) oxidized almost as rapidly at pH = 7 as at pH = 8.5 but developed much less rapidly at the lower pH. On the other hand, Elon
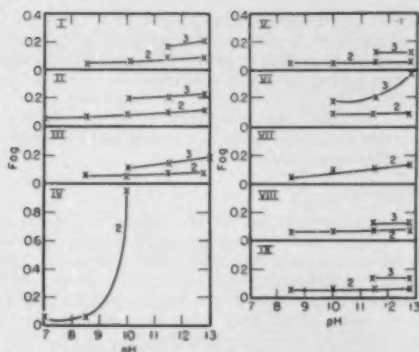
Fig. 4. Selectivity of Development. The fog obtained at constant image development (density = 2.0 or density = 3.0) is plotted as a function of the pH. With most agents the selectivity decreases slightly as the pH is raised. The high fog of No. IV has been attributed to the presence of a primary aliphatic amine in the molecule.

developed only 50 per cent more rapidly at the pH of 12.8 than at 11.5, but oxidized at nearly 4 times the rate. A peculiar inversion was obtained with the hydroxyethyl (III) and sulfomethyl (V) compounds, which actually oxidized somewhat more slowly at 12.8 than at 11.5. This leveling-off, or slight inversion, was obtained for both hue and activity and proved reproducible.

5. Solubility

The solubility of the developing agents in a high-salt solution of moderate alkalinity (pH = 10.0) is given in Table III. Nearly all of these compounds were more soluble than I and II, the conventional agents, and were not precipitated by the addition of hydroquinone, which forms the sparingly-soluble "metoquinone" with II. In spite of good solubility shown here at a pH of 10, the solubility of the agent, VIII, was very modest at pH values of 9 and lower.

Discussion

1. Development and the Ionic Charge Theory

The developing properties of these paraminophenols divides them into two broad classes: Group (a) in which the substituents are non-ionic in character, includes agents I, II, III, IV, and VIII, while Group (b), comprising those substituted by sulfonic and carboxylic acid groups includes Nos. V, VI, VII, and IX. The distinction between these groups is to be explained by assuming that Group (a) acts principally as singly charged ions, while Group (b) develops as doubly charged ions. These differences are seen both in (1) induction period, and (2) the pH response.

Group (a) has, in general, brief induction periods. The curves of Figure 2 may be extrapolated to show that, except for the most restrained pH conditions, development is initiated in the range of 0.25 to 2 minutes. But with Group (b), induction periods of from 4 to 16 minutes are not uncommon, although others are of the order of 1 minute.

Table III

SOLUBILITY

Agent	Grams per Liter	Precipitated by Addition of Hydroquinone
I.	6	No
II.	6	Yes
III.	30	No
IV.	Over 100	No
V.	Over 100	No
VI.	60	—
VII.	60	—
VIII.	20	No
IX.	Over 100	Yes

These long induction periods are similar to those found for the hydroquinones which, except in the most alkaline solutions, required from 2 minutes to 2 hours to initiate development. The long induction period of hydroquinone and of glycine (VI) has been explained by James[2] in terms of the difficulty of the more highly charged ions in penetrating the layer of negatively charged bromide ions surrounding the silver halide grain. He has shown on kinetic basis that the doubly charged ion would need to be present in 18 times as great a concentration as the singly charged ion to initiate development as effectively.
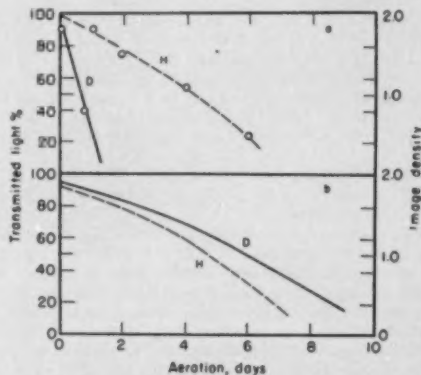

Fig. 5. Aeration Comparison. The aeration properties of (a) hydroquinone, and (b) Elon, are compared at a density of 10.0 with regard to image density produced (D) and the hue (H) of the solution following exposure in unstoppered flasks. Note that the hydroquinone loses activity rapidly but discolors only slowly, while the Elon discolors at about the same rate at which it loses activity. The sensitometric strips were developed in the hydroquinone developer for 14 minutes, and in the Elon developer for 4 minutes.

As the alkalinity is increased, the agents of Group (a) increase smoothly in activity over a wide pH range (Figure 3), while those of Group (b) are strongly affected by pH. The pH response of glycine, No. VI, closely resembles that of hydroquinone, only weak development being noted at pH of 8.5, which rapidly increases as the pH is raised to 11.5, but beyond this value the increase in rate is slight.

Table IV

DEVELOPING RATE

(Slope of Density : Log-Time Curve)
(ΔD/1.0 log t)

Agent	7.0	8.5	10.0	11.5	12.8
			Slope at pH =		
I.	..	1.32	2.57	2.60	2.60
II.	1.32	1.37	2.57	2.60	2.64
III.	1.40	1.40	2.57	2.57	2.60
IV.	0.78	1.09	2.60	..	..
V.	..	..	1.82	2.52	2.52
VI.	..	..	2.57	3.0	3.4
VII.	..	2.5	2.2	2.55	3.3
VIII.	..	0.78	1.28	1.97	2.6
IX.	..	1.65	1.63	2.25	2.65
Hydroquinone	..	..	3.3	3.3	3.3
Hydroquinone monosulfonate	..	..	..	4.1	4.1
X*	..	..	0.8	..	3.3

* N-Methyl-N-(β-sulfonamidoethyl)-p-aminophenol.

2. Significance of Slope of Density : Log-Time Curves

The ionic charge theory has been useful in explaining the differences in induction period and in pH response of the various agents. It is also applicable to a study of the slopes of the density : log-time curves of Figure 2. The values of these slopes, or "developing rates" have been entered in Table IV, as an aid to this discussion. It will be seen that the most common value of slope is about 2.6 (2.58 ± 0.07, average of 17 curves). This appears to characterize development by monovalent para-aminophenol, much as the value of 3.3 characterized the hydroquinones. Other slope values obtained were that of 1.35 for the paraminophenols of Group (a) used at pH values of 8.5 and lower, and that of 3.3 for the glycines (VI and VII) used at a pH of 12.8. The lower value might be considered to typify development by the un-ionized aminophenols, since a pH of 8.5 is far below their pK value (indicated previously as about 10.3), and ionization of only 1 molecule in 500 would be anticipated. The absence of these low slope values in Group (b) agents, which contain ionic substituents, and should not therefore present an un-ionized form, would bear out this hypothesis. It is interesting that the glycines, under the highly alkaline conditions, gave the same slope as the hydroquinones, since they also would be expected to be doubly charged.

In spite of these correlations, there are many examples where the slope value does not appear to correspond to the ionic state anticipated. Agents IV and VII have produced much flatter curves than the 1.35 value, and a number of values intermediate between the 1.35 and 2.6 slopes are evident. These may be merely transitory slopes indicating partial ionization, but more experimental data would be necessary to confirm this. On the contrary, the slopes in many instances are rigidly fixed over a wide range and do not show a change in slope corresponding to ionization:

A particularly interesting p-aminophenol was recently investigated by James,[4] and marked changes in rate related to a change in character from a monovalent to divalent developing ion. Curves obtained for this agent, N - methyl - N - (β - methylsulfonamidoethyl) - p - aminophenol, for the developer formula, emulsion, and condi-

tions of these tests are shown in Figure 7. Note the strong change of slope from 0.8 at pH = 10 to 3.3 density units per log-time unit at pH = 12.8, and the change of induction period, by nearly a factor of 10. This is a particularly clear-cut case of the trends of the agents of Figure 2, but note also the curves of Agent VII, which has certain structural units in common with the sulfonamidoethyl compound.

3. Selectivity

The selectivity of all of the agents is remarkably good with this positive material, even without bromide, with the exception of the aminoethyl compound already discussed. The lower fogging propensity of the aminophenols as compared with the hydroquinones is in line with the work of Abribat, Pouradier, and David[5] comparing Elon (II) and hydroquinone, but is contrary to the results obtained by Levenson,[6] particularly with negative films, who found hydroquinone to give less fog
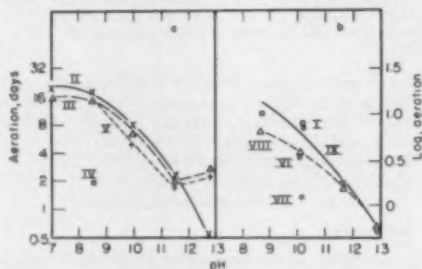

Fig. 6. Aeration Life vs. pH. The life, measured as days before the activity of the developer decreases to the point where one half of the original image density is produced, is plotted in a logarithmic scale to include the wide range of values. Note the resistance of Agents III and V to aeration at high pH. Also compare with the developing-rate curves of Fig. 3.

than Elon. The addition of bromide (0.01 mole per liter) where tested, further increased the selectivity, raising contrast and reducing emulsion speed. When development time was prolonged to match densities, the bromided developers produced about one third more contrast and about half the emulsion speed of the unbromided developers, much as found earlier for the hydroquinones. The various paraminophenol developers were only slightly less sensitive to bromide than the hydroquinone developers of equal activity level.

4. Oxidation

Development may be considered as oxidation of the agent by silver bromide (or other halide), whereas on exposure to air, aerial oxygen is the oxidizing agent. A comparison of Figures 3 and 6 shows how different these mechanisms are. The differences between the pH response to development and aerial oxidation of Agents II and III has already been pointed out. Thus, oxidation was little increased by raising the pH from 7 to 8.5, but development was greatly accelerated, and at the high pH range other discrepancies were evident. It is also
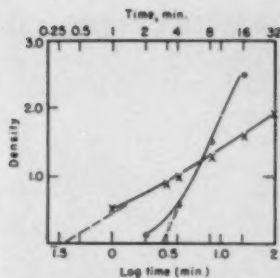
94

Table V

Fig. 7. Developing Properties of N Methyl - N (β - Amino-sulfonamidoethyl) - p-aminophenol. Note the strong change of both slope and induction period with pH. The curve marked with X's is for pH = 10.0, that with circles, for pH = 12.8.

Table V

DEVELOPERS OF MATCHED ACTIVITY

Agent	pH	Fog	Gamma	Emulsion Speed (%)	Aeration Life (Days) Activity	Aeration Life (Days) Hue
I.	10.1	0.06	2.0	80	8	8
II.	9.0	.07	2.0	85	14	10
III.	9.4	.06	...	80	8	6
IV.	9.6	.50	...	80	1-	1-
V.	10.8	.06	...	....	2.5	1.7
VI.	10.5	.10	2.0	80	4	5
VII.	11.0	.06	...	110	1.5	1.5
VIII.	11.3	.08	...	....	1.7	1.4
IX.	10.8	.06	...	....	4	0.9
Hydroquinone	10.5	.16	2.0	85	0.25	2.5

interesting to intercompare the several agents. Thus, III, V, I, and IX oxidized at about the same rate as Elon (II), but the developing rates of these agents differed by a factor of as much as 5 times, and Agents VI, VIII, and especially IV and VII oxidized appreciably more rapidly than II, but developed less actively.

5. Comparison at Equal Activity

The comparisons made so far have already been based on a fixed pH level. Very interesting results are obtained if the basis of comparison is, instead, one of equal activity level. This is done in Table V, where the properties of developers requiring 8 minutes to reach a density of 2.0 are entered. This development is achieved at a pH of 9.0 with Elon (II), the most active of the developers, while with the least active, an elevation to a pH of about 11 is necessary. The fog, contrast, and emulsion speed of these developers are then quite well matched, but the aeration life differs widely, those developers operating at the high pH level showing much shorter lives.

6. Practical Considerations

The commercial importance of Elon (II) appears well justified in these comparisons. It is the most active of any of the agents tested and its activity increases smoothly over a wide pH range. But in spite of its activity, it has equalled or excelled the other agents in resistance to oxidation under normal conditions. However, a number of other agents were more soluble than Elon (see Table III), while III and V were more resistant to oxidation at high pH. Some of the less active agents appear to produce less fog than Elon, but this advantage largely disappears when the pH is adjusted to match developing activity (Table V).

Agent III, the hydroxyethyl-p-aminophenol, is the next most interesting. It is only slightly less active than Elon (II), while its high solubility offers promise for concentrated developers, and it shows a singular resistance to oxidation at very high pH. The hydroxyethyl-p-aminophenol has been the subject of a patent,[7] and has had some commercial application.

Glycine (VI) finds occasional proponents, but this work would do little to affirm its usefulness as a single developing agent. It is active only in strongly alkaline solution and is then sensitive to slight changes in alkalinity. At very high pH levels, it loses much of its selectivity, producing dichroic fog and infectious development.

Chlorohydroquinone was previously shown to be considerably more active than hydroquinone, particularly at low pH.[1] The low activity of the chlorinated N-methyl-p-aminophenol sulfate (VIII) is therefore surprising. Similarly, 2-chloro-4-aminophenol has been found to have but 20 per cent of the activity of paraminophenol at a pH of 10. These differences are probably subject to explanation in terms of the ionic theory of development. Development is possible with the hydroquinones only as ionization occurs, and chlorination has increased ionization (lowered the pK value), and extended the range of development. But the aminophenols are apparently capable of development without ionization, and the introduction of further ionization has interfered with the normal development mechanism rather than extended it.

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USES OF KODALITH FILM IN THE EXAMINATION OF QUESTIONED DOCUMENTS

Joseph Tholl*

Kodalith emulsions, which are designed for certain kinds of reproduction work in the graphic arts, have proved to be of value in the examination of questioned documents. The unique effectiveness of Kodalith film in this field is due to its extremely high contrast, its sensitivity restricted to the blue and near ultra-violet parts of the spectrum and its ability, through modified processing, to record and build up intermediate tones which are otherwise flat or indistinguishable. Consequently, Kodalith film emulsions with their fine grain, their spectral sensitivity and selective behaviour bring out many kinds of obscure document evidence with clarity and brilliance.

Kodalith film is not necessarily better nor a good substitute for lower contrast panchromatic emulsions but it does have many unique applications in the document field. Also, it is well suited for reflected ultraviolet photography. In adapting Kodalith film to the photography of questioned documents it was found necessary to use, instead of the high contrast paraformaldehyde developer, a much softer though still energetic type of developer like D-72. The use of D-85 was not practical, with a few exceptions, because the high contrast at the expense of detail eliminates many vital intermediate tones. Given suitable development Kodalith film provides a valuable means for the detection, decipherment and demonstration of many kinds of physical evidence such as faint, obscure and erased written and printed matter; impressions transferred from another sheet; tampered paper surfaces; faded photographs and documents; the differentiation and identification of paper samples (with ultraviolet).

The proportional, intensifying-like action of Kodalith film is illustrated in Figure 1 showing a badly faded, old photograph which has been copied both on a medium

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contrast orthochromatic film and on Kodalith film. The overall increase in both contrast and detail by use of the Kodalith negative typifies the behaviour of this material with respect to various kinds of document evidence where tone separation and contrast must be increased in order to effect legibility or decipherment.
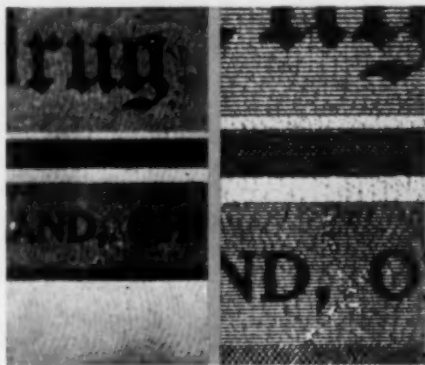

Fig. 2. Enlargement (2½X) of fine lithographed lines from a panchromatic film on the left compared to 4X enlargement of a Kodalith negative of the same subject.

Enlargements of Kodalith Negatives

Kodalith negatives when critically sharp and correctly developed will retain their wiry character at a considerable degree of enlargement. The respective enlarging qualities of Kodalith film and a medium fine grain panchromatic film are demonstrated by negatives made of the same subject (Figure 2). The fluorescence ultraviolet photograph in Figure 2, made from a panchromatic negative, shows a noticeable loss of definition at two and one-half diameters enlargement while a Kodalith film negative made under the same conditions shows no loss of definition at four diameters. The fine lines of the lithographed form in this case provided a critical test for both recording and enlargement.

The brilliance and wiry quality of Kodalith film enlargements are indispensable requisites for bringing out many forms of document evidence such as mechanical erasures and obscure markings. Figure 3 made from a
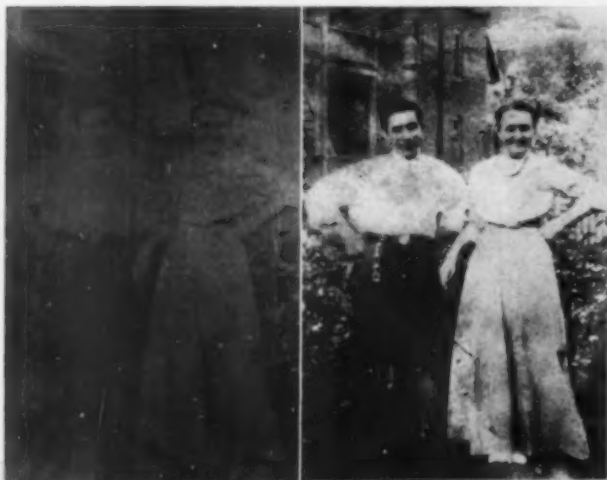

Fig. 1. Copy of old, badly faded photograph. The reproduction on the left is from a medium contrast ortho film negative, fully developed in D-72. The print on the right is from a Kodalith film negative, also developed in D-72.

Fig. 3. Erasure and alteration. Enlarged 10× from Kodalith negative.

slightly greater than life size Kodalith negative ($1^1/_2$ X) reveals, even at ten diameters print enlargement, a remarkable degree of depth, textural relief, and definition. Each torn fibre, the paper texture, every depression and projection is brought out with extreme clarity. The ability of the Kodalith film to reproduce paper textures and accentuate evidences of tampering has been demonstrated by many examples of sidelighted photographs of mechanical erasures.

Indentations, and markings transferred from another sheet of paper can be made quite legible through the use of Kodalith film and properly placed sidelights (Figure 4). Because of the high contrast and fine grain qualities of the Kodalith film illustrations it is possible, through this medium, to obtain with the use of ordinary equipment results that compare favorably with those secured from more involved photo-micrography set-ups. Inasmuch as many ink and pencil pigments appear dark or black in the Kodalith photograph it is often possible to decipher mechanical erasures without the use of special infrared and ultraviolet photography. Decipherment in such a case results where the embedded pencil and ink fragments are sharply outlined in black against the fiber-like detail of the paper surface; also, the inden-

Fig. 4. Kodalith film photograph of markings impressed from one sheet of paper to another sheet.
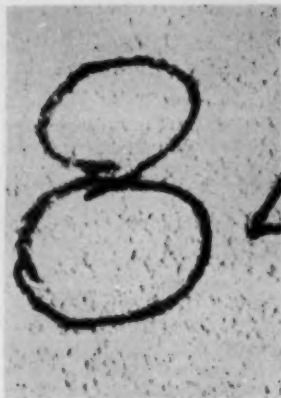
tations are brought out and made continuous through sharply etched shadows and highlights. Here the high contrast of the Kodalith film picks out the fragments of pigment and outlines the indentations (where they exist) while the selective behavior of this emulsion brings out the vital intermediate tones in the paper.

Reproduction and Decipherment of Pencil Writing

The litho type films are invaluable for the photography and demonstration of questioned documents which are executed in pencil; such writing might be the faint, worn, light writing on wills and anonymous letters and altered portions of receipts and agreements. In all such cases Kodalith film performs many useful functions which include: (1) the building up of essential contrast and density in obscure or erased pencil writing; (2) a selective action which differentiates many pencil pigments; (3) the heavier reproduction of photographically flat pigments without the loss of important paper detail.

In a recent Probate Court matter involving a number of faint, worn, pencil entries Kodalith film proved to be equally effective as Infrared film for increasing the density of the almost illegible writing. In another case, where anonymous pencil writing was made abnormally light as a means of concealment, Kodalith film provided a darker, more legible reproduction which could be more readily identified.

Kodalith film is quite as selective in the case of pencil pigments as infrared film. Even where deep blacks are registered on the print (Figure 3) the negative image may contain considerable detail which can be brought out by lighter printing or softer processing. In Figure 5 a lighter print reveals how the number "3" was altered into an "8" with another pencil.

The Reproduction of Light Carbon Impressions

During a recent investigation a receipt book was found containing several hundred duplicates on which the car-

bon impressions were a very faint blue. This writing, which was the principal evidence in a notorious criminal prosecution by the State, was found difficult to examine or photograph by reason of its irregularity, color, and lightness. This dilemma was solved by the use of Kodalith film and process development (D-85) which created sufficient contrast and continuity so that the faint, irregular carbon impressions could be enlarged without losing their form. It was then possible to construct comparison charts which established the identity of the questioned writing. These charts, in two successive trials, were bitterly attacked by defense counsel but each time were instrumental in securing a conviction.

Technique

EXPOSURE

It was found, generally, that where developers other than D-85 were used the exposure for Kodalith film was about one-fourth of that used in the case of process development. Some document subjects exposed in as little as two seconds at f/16 with Photoflood lighting. Reflected ultraviolet exposures were surprisingly short.

DEVELOPMENT

The Elon-hydroquinone-carbonate type of developer, such as D-72, was found to be more effective than other developers. Contrast was increased or decreased either by changing the proportion of developer ingredients or by dilution. The fine grain of Kodalith film makes the use of special fine grain developers unnecessary. Tests have proven that the more energetic D-72 developer was more effective than DK-20 for use with Kodalith film.
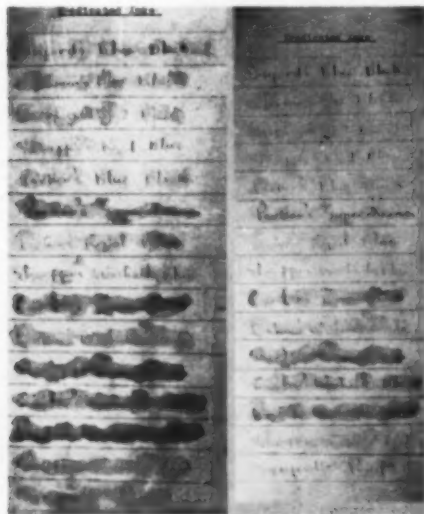

Fig. 6. Reflected ultraviolet photographs of a number of eradicated inks made from Kodalith film (left) and ortho film (right). The latter is flatter and shows less detail.

LIGHTING

Just as in other kinds of photographic recording the lighting is manipulated in accordance with the nature of the subject. Cross lighting is used where texture is not a factor. Cross lighting minimizes distracting textural details and allows tonal values to be recorded. Various degrees of sidelighting bring out texture and depth in evidence such as mechanical erasures and impressed writing. Focussed or concentrated lightings give a maximum of sharpness, depth and relief. It is apparent from the various illustrations used that any lighting will give a more pronounced effect with Kodalith than with other films.

EQUIPMENT

All of the illustrations in this paper were made with ordinary equipment which included a 4 × 5 Speed-Graphic camera with a 127 mm Ektar lens and Photoflood lighting. A cold quartz type lamp was used for the ultraviolet photographs.
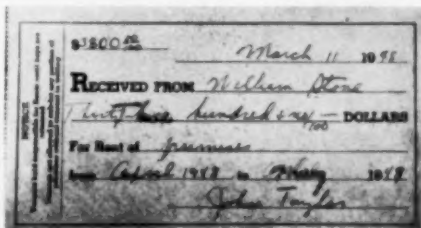

Fig. 7. Reflected ultraviolet photograph made with Kodalith film showing fraudulent interlineations and chemical erasures on a receipt.

Kodalith Ultraviolet Photography

Kodalith film is particularly well suited for ultraviolet photography. The effectiveness of the Kodalith emulsion for ultraviolet recording results from (1) its high contrast which overcomes the flattening effect the ultraviolet radiations have on other film emulsions; (2) its high sensitivity to the near ultraviolet which renders it a selective recording medium; (3) the thin emulsion layer which contains less ultraviolet-opaque gelatin than do the thicker emulsions. As a result of all these factors there is great brilliance, less objectionable fogging of the negative, and a greater latitude of exposure.

Many eradicated permanent inks and washable inks can be more positively deciphered by photographing on Kodalith rather than on commercial films. The excellence of Kodalith film for this purpose is shown in Figure 6 where practically every eradicated specimen of ink writing has been more or less restored photographically. A comparison in Figure 6 of the part made with Kodalith film and the part made with orthochromatic film demonstrates the superior recording possibilities of the former.

Alterations in a questioned receipt are clearly revealed by reflected ultraviolet photographs on Kodalith film in Figure 7. It can be seen that the ink used for the fraudulent interlineations has a relatively higher absorption of ultraviolet, recording as a dark shade whereas the original ink has a higher relative transmission and registers as a lighter shade.

The exposures for the Kodalith film pictures by ultraviolet from a cold quartz type lamp were quite short. The average exposure was 15 seconds at f/11. Exposures for fluorescence recording took a hundred times longer exposure.

Special Applications for Kodalith

PHOTOMICROGRAPHS

It has already been demonstrated how the fine grain and brilliant projection qualities of the Kodalith negative make possible unusually sharp, revealing enlargements from negatives of relatively small magnifications ($1\frac{1}{2}\times$ to $10\times$). Kodalith macrophotographs at greater magnification of mechanical erasures, embossures and tampered paper surfaces make effective court exhibits because of their accentuated recording.

BAS-RELIEF PHOTOGRAPHS

With certain types of mechanical erasures and impressed markings the illusion of depth may be useful in bringing out hidden or obscure details. Weak, variously processed positives made on Kodalith film and placed in slightly off-set register with a negative-will give a third dimensional effect. In a particularly stubborn case where typewriting had been cleverly erased it was possible by this method to bring out the erased word "all" which had been obliterated and superimposed with the figure "$\frac{1}{2}$."

TEST PLATES

In the examination and technical presentation of handwriting and typewriting peculiarities the use of trans-
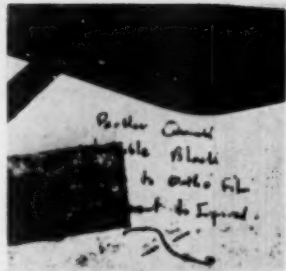

Fig. 8. Shadowgraph made through six thicknesses of paper. Kodalith film processed in D-85.

parent measuring and comparison plates may be imperative. These instruments can be copied to scale on Kodalith film from original drawings or book illustrations.

SHADOWGRAPHS

Wherever there is any transmission of light through a relatively opaque substance such as a heavy envelope it may be possible to secure an impression of the enclosure by placing the unopened envelope in a printing frame in contact with a sheet of Kodalith film. In Figure 8 Kodalith film, developed in D-85, has recorded writing enclosed in six thicknesses of paper. It is also practical by this method to examine suspected letters for evidences of forced opening without cutting open the envelope.

TRANSMITTED LIGHT PHOTOGRAPHS

Kodalith film will give sharp, brilliant transmitted light studies of questioned documents which will allow a considerable degree of enlargement. For this type of photograph the document should be placed in the printing frame with the printed or written side adjacent to the emulsion. A 10-watt lamp should be used for lighting and D-72 for development.

Photographic Technique for Professionals

TITLING PHOTOGRAPHIC PRINTS

A letter from a PSA member, published in the July 1952 issue, asked for suggestions for adding captions to 8 X 10 photographic prints. The problem was to provide neat, legible print titles without spending the time needed to prepare a photographic negative of the legends.
The following comments have been received and are published for the interest and information of other photographers who may be confronted with a similar problem.

PHOTOGRAPHIC METHODS ARE USED IN HOLLYWOOD

I undertook a great number of inquiries regarding this problem of placing titles on photographic prints with local people of Hollywood studio still and publicity departments, as well as representatives in the field of professional photographers. In most instances it seems that the caption or explanatory lettering is either put on the back of the print or it is glued as a separate item to the lower margin of the print in a folding type arrangement, which permits to pull the portion of the attachment inscribed into place so that the title can be read while the print is being inspected, whereafter the piece can be folded back to become invisible.

Most of the studios, in executing the copyright inscription for their photographic prints, use the technique of shooting the

necessary wording from a title board onto process panchromatic film, also commercial or litho film. The developed negative is then mounted together with the pictorial negative by cutting out from the pictorial negative a suitable portion from the least objectionable section of the film negative for insertion of the lettering material.

Techniques of optical superimposition are of course also used in title cameras, a method that gives excellent results, but is of very limited use, since few, if anyone, could afford cameras or equipment of that type.

It is my understanding that integrated captions of prints are more and more abandoned for the very reason that such illustrations are too frequently used for publication in magazines and newspapers, and the unavoidable reduction in size from the original and the degradation in quality present a serious problem of rendering such captions readable.

HERBERT MEYER
Hollywood, Calif.

FAST TITLING METHOD USING ELECTRIC TYPEWRITER

In current PS&T there is inquiry about fast captioning of photographic prints. No mention is made as to whether they want black on white or whether white on black will do.

Old time fast trick that we use for fast identifications is this: take sheet of thin acetate (clear film will do); use electric typewriter ribbon (*black* carbons); take out acetate without smudging, slick piece of clear Scotch tape over lettering to prevent smudging; attach to negative or edge of easel and print thru. Of course this gives white letters on black strip—but it's fastest thing I've seen.

Only faster thing is to label all subjects BEFORE making picture!

DAVID B. EISENDRATH, JR.
Brooklyn, N. Y.

BOSTON UNIVERSITY USES SEVERAL METHODS

The captioning of photographs for technical reports has long been a problem in our laboratory. We have used several methods, and are constantly trying new ones. Unfortunately, just about all of these involve a photographic process in some form.

The oldest, and probably most expensive method, is to produce on high contrast film a negative of the text to be added to the photograph. We have found that in a large number of title jobs Kodabromide F-4 or F-5 paper may be used in place of more expensive Kodalith film. We expose Kodabromide F-4 with a ten inch lens stopped to f/32, for about 45 seconds with the copy illuminated by two #4 Photoflood lamps.

The original copy to be thus made into a paper or film negative can be produced in several ways. Ordinary typewriting does not reproduce well; electric typewriters are considerably better. Lettering done with a LeRoy pen copies very well. This may be also used on transparent tape for addition to the photographic negative for contact printing. This is one of the quickest methods, if white letters on a black background can be used.

One of the standard methods for producing copy to be photographed is by pasting up or Scotch-taping special photo-type letters. Negatives produced from these pasted-up lines must usually be carefully retouched to avoid showing lines between

the letters. A simpler and neater method of producing such copy, although more expensive at the outset, is by means of the phototype setting machines, such as the Coxhead Headliner. This produces in a few minutes a clean strip of lettering on white opaque 35mm film, or transparent 35mm film. The lettering may be either black on white or white on black. This equipment, with eight different type faces, cost about $700. For volume production of titles or printed material to be photographed this system probably would pay for itself in time saved.

There are many companies whose business it is to prepare technical reports. If an industrial organization has occasional demand for such service, or is handicapped by lack of drafting, photographic, or reproduction facilities, these companies offer excellent service. If so desired, these companies can produce masters for use on Multilith, Bruning, Ozalid, Ditto, or what-have-you.

One final thought: possibly Xerography could be used in direct printing on photographic paper. The absorption into the gelatin layer of the special powder might be a problem, but this would be the only good approach other than special typewriters that completely eliminate the wet photographic process.

Typing might be feasible if special inks were developed that would be absorbed readily into the paper gelatin coating. Perhaps this idea has already been exploited. Surface activators might do the trick.

HUTSON K. HOWELL
Boston, Mass.

KODAK BOOKLETS ON TITLING ARE AVAILABLE

I am wondering whether you are familiar with the recommendations we make in our Data Book "Professional Printing with Kodak Photographic Papers."

You mentioned that you knew no better way than setting captions in type. Most companies that have any activity at all in the preparation of display or sample print material have constant relations with the printer, so the problem of having the type set up and printed offers no great problem. I believe the preference for printing by typeset material goes back to the demand for a neat appearing caption. In some cases, this can be attained by hand lettering but, in my experience, typeset material of this kind has been cheaper than hand lettered material.

A. L. TERLOUW
Rochester, N. Y.

PHOTOGRAPHIC TITLES USED IN PENNSYLVANIA

I wonder if PSA Member, looking for a means of captioning prints, has tried copying his titles on Kodalith film or similar film made by other companies.

Titles can be printed by hand or typed, then copied to desired size of letters, larger or smaller. In typing titles, the type should be clean to give a clear impression on fair quality letter paper. For best results, I prefer a linotype impression or lettering by hand.

Titles are cut apart with the trimmer and fitted to the picture negative in the usual manner. I know of no other method that can be done more cheaply, neatly, or quickly than this.

RUSSELL E. JOHNSON
Wyomissing, Penna.